Combustion Science and Technology

A Comprehensive Chemical Kinetic Reaction Mechanism for Oxidation and Pyrolysis of Propane and Propene

Charles K. Westbrook [a]; William J. Pitz [a]
[a] Arizona State University,, Livermore, California

PLEASE SCROLL DOWN FOR ARTICLE

A Comprehensive Chemical Kinetic Reaction Mechanism for Oxidation and Pyrolysis of Propane and Propene

CHARLES K. WESTBROOK and WILLIAM J. PITZ   *Lawrence Livermore National Laboratory, Livermore, California 94550*

Abstract—A detailed chemical kinetic reaction mechanism is developed to describe the oxidation and pyrolysis of propane and propene. The mechanism consists of 163 elementary reactions among 41 chemical species. New rate expressions are developed for a number of reactions of propane, propene, and intermediate hydrocarbon species with radicals including H, O, and OH. The mechanism is tested by comparisons between computed and experimental results in shock tubes and the turbulent flow reactor. The resulting comprehensive mechanism accurately reproduces experimental data for pressures from 1 to 15 atmospheres, temperatures from 1000 to 1700 K, and fuel-oxidizer equivalence ratios from 0.066 to pyrolysis conditions. The mechanism also predicts correctly laminar flame properties for propane and propene, and detonation properties for propane.

INTRODUCTION

Propane is an important combustion fuel and is often used in studies of oxidation processes in laboratory burners, internal combustion engines, detonations, and many other environments. Unlike hydrocarbon fuels with simpler structures such as methane or ethane, the thermochemical and combustion properties of propane are similar in many ways to those of more complex practical fuels.

Relatively few detailed modeling studies of propane and propene combustion have appeared. Most of these have treated only pyrolysis, and only a few (Warnatz, 1981, 1983b; Westbrook and Pitz, 1983b) examined propane oxidation in laminar flames. In most of these previous studies, the detailed reaction mechanism was developed specifically for that one type of combustion environment. Therefore chemical species and elementary reactions not important for that application were generally discarded.

The present modeling study represents a continuation in the development of "comprehensive" reaction mechanisms (Westbrook and Dryer, 1981) for the combustion of hydrocarbon fuels. In this approach, mechanisms are intended to be applicable simultaneously to a wide variety of combustion regimes. Therefore, reactions and species which are important in any relevant application are retained. When this is done, the resulting mechanism can be used to predict combustion phenomena over wide ranges of operating conditions, without further modification. The development and testing in the present paper of this type of reaction mechanism for propane and propene combustion includes comparisons between numerical predictions and experimental data from shock tubes and the turbulent flow reactor, and the resulting mechanism has been used to simulate their combustion in laminar flames and detonation waves.

REACTION MECHANISM

The detailed reaction mechanism for pyrolysis and oxidation of propane and propene was constructed from an earlier mechanism for the oxidation of C_1 and C_2 species (Westbrook *et al.*, 1983a) by adding elementary steps describing reactions of C_3H_8 and its product species. The rates of these additional reactions were then varied within acceptable ranges to provide the best possible agreement between computed and experimental results. The final mechanism and rate expressions are summarized in Table I. Reverse rates are computed from the forward rates and the appropriate equilibrium constants (*JANAF*, 1970; Bahn, 1973). Reactions whose rates were determined by the present modeling study are identified. In addition, the rates of a number of other reactions were estimated for this study, but the sensitivity of the computed results to variations in their rates was too small to provide any confirmation of the assumed rate expressions, and these reactions are also appropriately identified in Table I.

For propane and propene, initiation reactions include

$$C_3H_8 = C_2H_5 + CH_3 \tag{94}$$

$$C_3H_6 = C_3H_5 + H \tag{149}$$

$$C_3H_6 = C_2H_3 + CH_3 \tag{161}$$
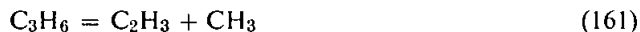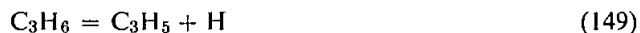
All three reactions are assumed to be at their high pressure limits, although high temperature shock tube studies (Burcat, 1975; Kiefer *et al.*, 1982; Simmie *et al.*, 1982; Al-Alami and Kiefer, 1983) indicate that they are somewhat pressure dependent under those conditions. The rate expression for Reaction 94 was initially taken from Tsang (1969) and Hautman *et al.* (1981), but modeling analysis of propane pyrolysis experiments of Chiang and Skinner (1981) to be discussed below led to a reduction of slightly more than 50 per cent in the pre-exponential A_{94}. The resulting rate expression in Table I is in reasonably good agreement with other determinations of k_{94} by Allara and Shaw (1980), Sundaram and Froment (1978), Chiang and Skinner (1981), Koike and Gardiner (1980), Simmie *et al.* (1982), and Al-Alami and Kiefer (1983), and is smaller by a factor of about 20 than the expressions of Trotman-Dickenson (1965) and Laidler *et al.* (1962). Alternative initiation reactions for C_3H_8 involving H atoms or H_2 molecules as products were not included, based on their estimated higher activation energies.

Two initiation reactions for propene decomposition have been considered extensively in the literature, Reactions 149 and 161. The rate expression for Reaction 149 was taken from Laidler and Wojciechowski (1960) and that for Reaction 161 from Chappell and Shaw (1968), and the pre-exponentials were varied to give the best agreement between computed and experimental results for product distributions in propene pyrolysis. Since the pyrolysis data chosen for analysis (Burcat, 1975) were all at temperatures around 1300–1400 K, this process really determines only the ratio of k_{149} to k_{161} at these temperatures, not their separate temperature dependences. Because of resonance stabilization energy of the allyl radical (McMillen and Golden, 1982), the bond dissociation energy of Reaction 149 is lower than that of Reaction 161 by approximately 10 kcal/mole, so it might be expected that rate expressions should include $E_{149} < E_{161}$ by 8–10 kcal/mole. Unfortunately, the temperature range and precision of the experimental data considered in this study were insufficient to deter-

TABLE I

Fuel oxidation mechanism. Reaction rates in cm^3-mole-sec-kcal units, $k = AT^n \exp(-E_a/RT)$

		Forward rate			Reverse rate			
	Reaction	$\log A$	n	E_a	$\log A$	n	E_a	Reference
1.	$H + O_2 \rightarrow O + OH$	14.34	0	16.79	13.24	0	0.68	Baulch et al., 1973a
2.	$H_2 + O \rightarrow H + OH$	10.26	1	8.90	9.92	1	6.95	Baulch et al., 1973b
3.	$H_2O + O \rightarrow OH + OH$	13.83	0	18.35	12.80	0	1.10	Baulch et al., 1973b
4.	$H_2O + H \rightarrow H_2 + OH$	13.98	0	20.30	13.34	0	5.15	Baulch et al., 1973b
5.	$H_2O_2 + OH \rightarrow H_2O + HO_2$	13.00	0	1.80	13.45	0	32.79	Baulch et al., 1973b
6.	$H_2O + M \rightarrow H + OH + M$	16.34	0	105.00	23.15	-2	0.00	Baulch et al., 1973b
7.	$H + O_2 + M \rightarrow HO_2 + M$	15.22	0	-1.00	15.36	0	45.90	Baulch et al., 1973b
8.	$HO_2 + O \rightarrow OH + O_2$	13.70	0	1.00	13.81	0	56.61	Lloyd, 1974
9.	$HO_2 + H \rightarrow OH + OH$	14.40	0	1.90	13.08	0	40.10	Baulch et al., 1973b
10.	$HO_2 + H \rightarrow H_2 + O_2$	13.40	0	0.70	13.74	0	57.80	Baulch et al., 1973b
11.	$HO_2 + OH \rightarrow H_2O + O_2$	13.70	0	1.00	14.80	0	73.86	Lloyd, 1974
12.	$H_2O_2 + O_2 \rightarrow HO_2 + HO_2$	13.60	0	42.64	13.00	0	1.00	Lloyd, 1974
13.	$H_2O_2 + M \rightarrow OH + OH + M$	17.08	0	45.50	14.96	0	-5.07	Baulch et al., 1973b
14.	$H_2O_2 + H \rightarrow HO_2 + H_2$	12.23	0	3.75	11.86	0	18.70	Baulch et al., 1973b
15.	$O + H + M \rightarrow OH + M$	16.00	0	0.00	19.90	-1	103.72	Moretti, 1965
16.	$O_2 + M \rightarrow O + O + M$	15.71	0	115.00	15.67	-0.28	0.00	Jenkins et al., 1967
17.	$H_2 + M \rightarrow H + H + M$	14.34	0	96.00	15.48	0	0.00	Baulch et al., 1973b
18.	$CO + OH \rightarrow CO_2 + H$	7.18	1.3	-0.77	9.23	1.3	21.58	Baulch and Drysdale, 1974
19.	$CO + HO_2 \rightarrow CO_2 + OH$	14.18	0	23.65	15.23	0	85.50	Baulch et al., 1976
20.	$CO + O + M \rightarrow CO_2 + M$	15.77	0	4.10	21.74	-1	131.78	Simonaitis and Heicklen, 1972
21.	$CO_2 + O \rightarrow CO + O_2$	12.44	0	43.83	11.50	0	37.60	Gardiner et al., 1971
22.	$HCO + OH \rightarrow CO + H_2O$	14.00	0	0.00	15.45	0	105.15	Bowman, 1970
23.	$HCO + M \rightarrow H + CO + M$	14.16	0	19.00	11.70	1	1.55	Westbrook et al., 1977
24.	$HCO + H \rightarrow CO + H_2$	14.30	0	0.00	15.12	0	90.00	Niki et al., 1969
25.	$HCO + O \rightarrow CO + OH$	14.00	0	0.00	14.46	0	87.90	Westenberg and de Haas, 1972
26.	$HCO + HO_2 \rightarrow CH_2O + O_2$	14.00	0	3.00	15.56	0	46.04	Baldwin and Walker, 1973
27.	$HCO + O_2 \rightarrow CO + HO_2$	12.60	0	7.00	12.95	0	39.29	Westbrook et al., 1977
28.	$CH_2O + M \rightarrow HCO + H + M$	16.52	0	81.00	11.15	1	-11.77	Dean et al., 1980
29.	$CH_2O + OH \rightarrow HCO + H_2O$	12.88	0	0.17	12.41	0	29.99	Atkinson and Pitts, 1978
30.	$CH_2O + H \rightarrow HCO + H_2$	14.52	0	10.50	13.42	0	25.17	Dean et al., 1980
31.	$CH_2O + O \rightarrow HCO + OH$	13.70	0	4.60	12.24	0	17.17	Bowman, 1975

Reaction	Forward rate			Reverse rate			Reference
	$\log A$	n	E_a	$\log A$	n	E_a	
32. CH_2O+HO_2 → $HCO+H_2O_2$	12.00	0	8.00	11.04	0	6.59	Lloyd, 1974
33. CH_4+M → CH_3+H+M	17.15	0	88.40	11.45	1	−19.52	Hartig et al., 1971
34. CH_4+H → CH_3+H_2	14.10	0	11.90	12.68	0	11.43	Baldwin et al., 1970
35. CH_4+OH → CH_3+H_2O	3.54	3.08	2.00	2.76	3.08	16.68	Zellner and Steinert, 1976
36. CH_4+O → CH_3+OH	13.20	0	9.20	11.43	0	6.64	Herron, 1969
37. CH_4+HO_2 → $CH_3+H_2O_2$	13.30	0	18.00	12.02	0	1.45	Skinner et al., 1972
38. CH_3+HO_2 → CH_3O+OH	13.51	0	0.00	10.00	0	0.00	Colket et al., 1977
39. CH_3+OH → CH_2O+H_2	12.60	0	0.00	14.08	0	71.73	Fenimore, 1969
40. CH_3+O → CH_2O+H	14.11	0	2.00	15.23	0	71.63	Peeters and Mahnen, 1973
41. CH_3+O_2 → CH_3O+O	13.68	0	29.00	14.48	0	0.73	Brabbs and Brokaw, 1975
42. CH_2O+CH_3 → CH_4+HCO	10.00	0.5	6.00	10.32	0.5	21.14	Tunder et al., 1966
43. CH_3+HCO → CH_4+CO	11.48	0.5	0.00	13.71	0.5	90.47	Tunder et al., 1966
44. CH_4+O_2 → CH_3+HO_2	12.00	0	0.40	13.88	0	58.59	Skinner et al., 1972
45. CH_3O+M → CH_2O+H+M	13.70	0	21.00	9.00	1	−2.56	Brabbs and Brokaw, 1975
46. CH_3O+O_2 → CH_2O+HO_2	12.00	0	6.00	11.11	0	32.17	Engleman, 1976
47. C_2H_6 → CH_3+CH_3	19.35	−1	88.31	12.95	0	0.00	Pacey, 1973
48. $C_2H_6+CH_3$ → $C_2H_5+CH_4$	−0.26	4	8.28	10.48	0	12.50	Clark and Dove, 1973
49. C_2H_6+H → $C_2H_5+H_2$	2.73	3.5	5.20	2.99	3.5	27.32	Clark and Dove, 1973
50. C_2H_6+OH → $C_2H_5+H_2O$	9.94	1.05	1.81	10.23	1.05	23.94	Tully et al., 1983
51. C_2H_6+O → C_2H_5+OH	13.40	0	6.36	12.66	0	11.23	Herron and Huie, 1973
52. C_2H_5+M → C_2H_4+H+M	15.30	0	30.00	10.62	0	−11.03	Olson et al., 1979
53. $C_2H_5+O_2$ → $C_2H_4+HO_2$	12.00	0	5.00	11.12	0	13.70	Westbrook, 1979
54. $C_2H_4+C_2H_4$ → $C_2H_5+C_2H_3$	14.70	0	64.70	14.17	0	−2.61	Benson and Haugen, 1967
55. C_2H_4+M → $C_2H_2+H_2$	16.97	0	77.20	12.66	1	36.52	Westbrook et al., 1983a
56. C_2H_4+M → C_2H_3+H+M	18.80	0	108.72	17.30	0	0.00	Westbrook et al., 1983a
57. C_2H_4+O → CH_3+HCO	12.52	0	1.13	11.20	0	31.18	Davis et al., 1972
58. C_2H_4+O → CH_2O+CH_2	13.40	0	5.00	12.48	0	15.68	Westbrook et al., 1983a
59. C_2H_4+H → $C_2H_3+H_2$	7.18	2	6.00	6.24	2	5.11	Westbrook et al., 1983a
60. C_2H_4+OH → $C_2H_3+H_2O$	12.68	0	1.23	12.08	0	14.00	Westbrook et al., 1983a
61. C_2H_4+OH → CH_3+CH_2O	12.30	0	0.96	11.78	0	16.48	Westbrook et al., 1983a
62. C_2H_3+M → C_2H_2+H+M	14.90	0	31.50	11.09	1	−10.36	Benson and Haugen, 1967

Table I (continued)

Reaction		Forward rate			Reverse rate			Reference
		log A	n	E_a	log A	n	E_a	
63. $C_2H_3+O_2$	$\rightarrow C_2H_2+HO_2$	12.00	0	10.00	12.00	0	17.87	Westbrook et al., 1983a
64. C_2H_2+M	$\rightarrow C_2H+H+M$	14.00	0	114.00	9.04	1	0.77	Jachimowski, 1977
65. $C_2H_2+O_2$	$\rightarrow HCO+HCO$	12.60	0	28.00	11.00	0	63.65	Gardiner and Walker, 1968
66. C_2H_2+H	$\rightarrow C_2H+H_2$	14.30	0	19.00	13.62	0	13.21	Browne et al., 1969
67. C_2H_2+OH	$\rightarrow C_2H+H_2O$	12.78	0	7.00	12.73	0	16.36	Vandooren and Van Tiggelen, 1977
68. C_2H_2+OH	$\rightarrow CH_2CO+H$	11.51	0	0.20	12.50	0	20.87	Vandooren and Van Tiggelen, 1977
69. C_2H_2+O	$\rightarrow C_2H+OH$	15.51	−0.6	17.00	14.47	−0.6	0.91	Browne et al., 1969
70. C_2H_2+O	$\rightarrow CH_2+CO$	13.83	0	4.00	13.10	0	54.67	Vandooren and Van Tiggelen, 1977
71. C_2H+O_2	$\rightarrow HCO+CO$	13.00	0	7.00	12.93	0	138.40	Browne et al., 1969
72. C_2H+O	$\rightarrow CO+CH$	13.70	0	0.00	13.50	0	59.43	Browne et al., 1969
73. CH_2+O_2	$\rightarrow HCO+OH$	14.00	0	3.70	13.61	0	76.58	Westbrook et al., 1977
74. CH_2+O	$\rightarrow CH+OH$	11.28	0.68	25.00	10.77	0.68	25.93	Mayer et al., 1967
75. CH_2+H	$\rightarrow CH+H_2$	11.43	0.67	25.70	11.28	0.67	28.72	Mayer et al., 1967
76. CH_2+OH	$\rightarrow CH+H_2O$	11.43	0.67	25.70	11.91	0.67	43.88	Peeters and Vinckier, 1975
77. $CH+O_2$	$\rightarrow CO+OH$	11.13	0.67	25.70	11.71	0.67	185.60	Peeters and Vinckier, 1975
78. $CH+O_2$	$\rightarrow HCO+O$	13.00	0.	0.00	13.13	0	71.95	Jachimowski, 1977
79. CH_3OH+M	$\rightarrow CH_3+OH+M$	18.48	0	80.00	13.16	1	−10.98	Westbrook and Dryer, 1979
80. CH_3OH+OH	$\rightarrow CH_2OH+H_2O$	12.60	0	2.00	7.27	1.66	25.31	Westbrook and Dryer, 1979
81. CH_3OH+O	$\rightarrow CH_2OH+OH$	12.23	0	2.29	5.90	1.66	8.35	Le Fevre et al., 1972
82. CH_3OH+H	$\rightarrow CH_2OH+H_2$	13.48	0	7.00	7.51	1.66	15.16	Westbrook and Dryer, 1979
83. CH_3OH+H	$\rightarrow CH_3+H_2O$	12.72	0	5.34	12.32	0	36.95	Westbrook and Dryer, 1979
84. CH_3OH+CH_3	$\rightarrow CH_2OH+CH_4$	11.26	0	9.80	6.70	1.66	18.43	Gray and Herod, 1968
85. CH_3OH+HO_2	$\rightarrow CH_2OH+H_2O_2$	12.80	0	19.36	7.00	1.66	11.44	Aronowitz et al., 1979
86. CH_2OH+M	$\rightarrow CH_2O+H+M$	13.40	0	29.00	16.69	−0.66	7.58	Westbrook and Dryer, 1979
87. CH_2OH+O_2	$\rightarrow CH_2O+HO_2$	12.00	0	6.00	17.94	−1.66	28.32	Aronowitz et al., 1979
88. $C_2H_3+C_2H_4$	$\rightarrow C_4H_6+H$	12.00	0	7.30	13.00	0	4.70	Benson and Haugen, 1967
89. $C_2H_2+C_2H_2$	$\rightarrow C_4H_3+H$	13.00	0	45.00	13.18	0	0.00	Tanzawa and Gardiner, 1979
90. C_4H_3+M	$\rightarrow C_4H_2+H+M$	16.00	0	60.00	11.92	1	2.54	Tanzawa and Gardiner, 1979
91. $C_2H_2+C_2H$	$\rightarrow C_4H_2+H$	13.60	0	0.00	14.65	0	0.55	Tanzawa and Gardiner, 1979
92. C_4H_2+M	$\rightarrow C_4H+H+M$	17.54	0	80.00	12.30	1.0	−16.40	Tanzawa and Gardiner, 1979
93. C_2H_3+H	$\rightarrow C_2H_2+H_2$	13.30	0	2.50	13.12	0	68.08	Tanzawa and Gardiner, 1980

Table 1 (continued over)

C. K. WESTBROOK AND W. J. PITZ

Reaction		Forward rate			Reverse rate			Reference
		$\log A$	n	E_a	$\log A$	n	E_a	
94. C_3H_5	$\rightarrow CH_3 + C_2H_5$	16.23	0	84.84	10.18	1	-0.32	This study
95. $CH_3 + C_3H_8$	$\rightarrow CH_4 + iC_3H_7$	15.04	0	25.14	15.64	0	32.12	Hautman et al., 1981
96. $CH_3 + C_3H_8$	$\rightarrow CH_4 + nC_3H_7$	15.04	0	25.14	15.64	0	32.12	Hautman et al., 1981
97. $H + C_3H_8$	$\rightarrow H_2 + iC_3H_7$	6.94	2	5.00	12.89	0	15.87	This study
98. $H + C_3H_8$	$\rightarrow H_2 + nC_3H_7$	7.75	2	7.70	12.96	0	14.46	This study
99. iC_3H_7	$\rightarrow H + C_3H_6$	13.80	0	36.90	13.00	0	1.50	Kerr, Trotman-Dickenson, 1959
100. iC_3H_7	$\rightarrow CH_3 + C_2H_4$	10.30	0	29.50	4.66	1	4.29	Kerr, Trotman-Dickenson, 1959
101. nC_3H_7	$\rightarrow CH_3 + C_2H_4$	13.98	0	31.00	8.34	1	5.79	This study
102. nC_3H_7	$\rightarrow H + C_3H_6$	14.10	0	37.00	13.00	0	1.50	Jackson and McNesby, 1961
103. $iC_3H_7 + C_3H_8$	$\rightarrow nC_3H_7 + C_3H_8$	10.48	0	12.90	10.48	0	12.90	Berkley et al., 1969
104. $C_2H_3 + C_3H_8$	$\rightarrow C_2H_4 + iC_3H_7$	11.00	0	10.40	11.12	0	17.80	Hautman et al., 1981
105. $C_2H_3 + C_3H_8$	$\rightarrow C_2H_4 + nC_3H_7$	11.00	0	10.40	11.12	0	17.80	Hautman et al., 1981
106. $C_2H_5 + C_3H_8$	$\rightarrow C_2H_6 + iC_3H_7$	11.00	0	10.40	10.56	0	9.93	Trotman-Dickenson, 1965
107. $C_2H_5 + C_3H_8$	$\rightarrow C_2H_6 + nC_3H_7$	11.00	0	10.40	10.56	0	9.93	Trotman-Dickenson, 1965
108. $C_3H_8 + O$	$\rightarrow iC_3H_7 + OH$	6.70	2	3.00	5.52	2	7.41	This study, est.
109. $C_3H_8 + O$	$\rightarrow nC_3H_7 + OH$	6.70	2	3.00	5.52	2	7.41	This study, est.
110. $C_3H_8 + OH$	$\rightarrow iC_3H_7 + H_2O$	8.68	1.4	0.85	8.93	1.25	22.37	Tully et al., 1983
111. $C_3H_8 + OH$	$\rightarrow nC_3H_7 + H_2O$	8.76	1.4	0.85	9.01	1.25	22.37	Tully et al., 1983
112. $C_3H_8 + HO_2$	$\rightarrow iC_3H_7 + H_2O_2$	12.70	0	18.00	12.01	0	8.43	This study, est.
113. $C_3H_8 + HO_2$	$\rightarrow nC_3H_7 + H_2O_2$	12.70	0	18.00	12.01	0	8.43	This study, est.
114. $C_3H_6 + O$	$\rightarrow C_2H_4 + CH_2O$	13.77	0	5.00	13.76	0	86.67	This study, est.
115. $iC_3H_7 + O_2$	$\rightarrow C_3H_6 + HO_2$	12.00	0	5.00	11.30	0	17.48	This study, est.
116. $nC_3H_7 + O_2$	$\rightarrow C_3H_6 + HO_2$	12.00	0	5.00	11.30	0	17.48	This study, est.
117. $C_3H_8 + O_2$	$\rightarrow iC_3H_7 + HO_2$	13.60	0	47.50	12.31	0	-3.71	Walker, 1975
118. $C_3H_8 + O_2$	$\rightarrow nC_3H_7 + HO_2$	13.60	0	47.50	12.31	0	-3.71	Walker, 1975
119. $C_3H_6 + OH$	$\rightarrow C_2H_5 + CH_2O$	12.90	0	0.00	13.66	0	17.35	Cathonnet et al., 1981
120. $C_3H_6 + O$	$\rightarrow C_2H_5 + HCO$	12.55	0	0.00	11.85	0	29.92	This study, est.
121. $C_3H_6 + OH$	$\rightarrow CH_3 + CH_3CHO$	11.54	0	0.00	11.44	0	20.40	This study
122. $C_3H_6 + O$	$\rightarrow CH_3 + CH_3CO$	13.07	0	0.60	12.25	0	38.37	This study, est.
123. $CH_3CHO + H$	$\rightarrow CH_3CO + H_2$	13.60	0	4.20	13.25	0	23.67	Warnatz, 1981
124. $CH_3CHO + OH$	$\rightarrow CH_3CO + H_2O$	13.00	0	0.00	13.28	0	36.62	Warnatz, 1981

Table I (continued)

	Reaction	Forward rate			Reverse rate			Reference
		$\log A$	n	E_a	$\log A$	n	E_a	
125.	$CH_3CHO+O \rightarrow CH_3CO+OH$	12.70	0	1.79	12.00	0	19.16	Warnatz, 1981
126.	$CH_3CHO+CH_3 \rightarrow CH_3CO+CH_4$	12.23	0	8.43	13.48	0	28.00	Warnatz, 1981
127.	$CH_3CHO+HO_2 \rightarrow CH_3CO+H_2O_2$	12.23	0	10.70	12.00	0	14.10	Colket et al., 1977
128.	$CH_3CHO \rightarrow CH_3+HCO$	15.85	0	81.78	9.58	1	0.00	Colket et al., 1977
129.	$CH_3CHO+O_2 \rightarrow CH_3CO+HO_2$	13.30	0.5	42.20	7.00	0.5	4.00	Colket et al., 1977
130.	$CH_3CO \rightarrow CH_3+CO$	13.48	0	17.24	11.20	0	5.97	Watkins and Word, 1974
131.	$C_3H_6+H \rightarrow C_2H_5+H_2$	12.70	0	1.50	12.18	0	17.70	This study
132.	$C_3H_6+CH_3 \rightarrow C_2H_5+CH_4$	10.95	0	8.50	11.87	0	25.18	Cvetanovic and Irwin, 1967
133.	$C_3H_6+C_2H_5 \rightarrow C_2H_5+C_2H_6$	11.00	0	9.20	5.00	0	56.77	Sundaram and Froment, 1978
134.	$C_3H_6+OH \rightarrow C_2H_5+H_2O$	12.60	0	0.00	7.18	0	69.69	This study, est.
135.	$C_3H_3+C_3H_5 \rightarrow iC_3H_7+C_3H_6$	11.60	0	16.20	11.30	0	6.50	Hautman et al., 1981
136.	$C_2H_6+C_3H_5 \rightarrow nC_3H_7+C_3H_6$	11.60	0	16.20	11.30	0	6.50	Hautman et al., 1981
137.	$C_3H_5 \rightarrow C_3H_4+H$	13.60	0	70.00	8.00	1	0.00	Amano and Uchiyama, 1963
138.	$C_3H_5+O_2 \rightarrow C_3H_4+HO_2$	11.78	0	10.00	11.08	0	10.00	This study
139.	$iC_4H_8 \rightarrow C_3H_5+CH_3$	19.18	-1	73.40	13.13	0	0.00	This study, est.
140.	$iC_4H_8 \rightarrow C_2H_3+C_2H_5$	19.00	-1	96.77	12.95	0	0.00	This study
141.	$iC_4H_8+O \rightarrow CH_3CHO+C_2H_4$	13.11	0	0.85	12.32	0	85.10	This study, est.
142.	$iC_4H_8+O \rightarrow CH_3CO+C_2H_5$	13.11	0	0.85	12.37	0	38.15	This study, est.
143.	$iC_4H_8+OH \rightarrow CH_3CHO+C_2H_5$	13.00	0	0.00	12.97	0	19.93	This study, est.
144.	$iC_4H_8+OH \rightarrow CH_3CO+C_2H_6$	13.00	0	0.00	12.99	0	32.43	This study, est.
145.	$C_3H_4+O \rightarrow CH_2O+C_2H_2$	12.00	0	0.00	12.03	0	81.73	This study, est.
146.	$C_3H_4+O \rightarrow HCO+C_2H_3$	12.00	0	0.00	10.47	0	30.82	This study, est.
147.	$C_3H_4+OH \rightarrow CH_2O+C_2H_3$	12.00	0	0.00	11.93	0	18.25	This study, est.
148.	$C_3H_4+OH \rightarrow HCO+C_2H_4$	12.00	0	0.00	11.77	0	33.81	This study, est.
149.	$C_3H_6 \rightarrow C_2H_5+H$	13.00	0	78.00	11.00	0	0.00	Laidler and Wojciechowski, 1960
150.	$C_2H_2+O \rightarrow HCCO+H$	4.55	2.7	1.39	2.70	2.7	12.79	Miller et al., 1983
151.	$CH_2CO+H \rightarrow CH_3+CO$	13.04	0	3.40	12.38	0	40.20	Michael et al., 1979
152.	$CH_2CO+O \rightarrow HCO+HCO$	13.00	0	2.40	11.54	0	33.50	Warnatz, 1981
153.	$CH_2CO+OH \rightarrow CH_2O+HCO$	13.45	0	0.00	13.44	0	18.50	Warnatz, 1981
154.	$CH_2CO+M \rightarrow CH_2+CO+M$	16.30	0	60.00	10.66	0	0.00	Miller et al., 1983
155.	$CH_2CO+O \rightarrow HCCO+OH$	13.70	0	8.00	10.86	0	8.00	Miller et al., 1983

Table 1 (continued over)

Reaction	Forward rate			Reverse rate			Reference
	log A	n	E_a	log A	n	E_a	
156. $CH_2CO + OH \rightarrow HCCO + H_2O$	12.88	0	3.00	11.03	0	11.00	Miller et al., 1983
157. $CH_2CO + H \rightarrow HCCO + H_2$	13.88	0	8.00	11.39	0	8.00	Miller et al., 1983
158. $HCCO + OH \rightarrow HCO + HCO$	13.00	0	0.00	13.68	0	40.36	Miller et al., 1983
159. $HCCO + H \rightarrow CH_2 + CO$	13.70	0	0.00	13.82	0	39.26	Miller et al., 1983
160. $HCCO + O \rightarrow HCO + CO$	13.53	0	2.00	13.92	0	128.26	Miller et al., 1983
161. $C_3H_6 \rightarrow C_2H_3 + CH_3$	15.80	0	85.80	10.00	1	0.00	This study
162. $C_3H_5 + H \rightarrow C_3H_4 + H_2$	13.00	0	0.00	13.00	0	40.00	This study, est.
163. $C_3H_5 + CH_3 \rightarrow C_3H_4 + CH_4$	12.00	0	0.00	13.00	0	40.00	This study, est.

All third body efficiencies are 1.0 except for the following:

$k_6(H_2O) = 20 k_6(N_2)$

$k_7(H_2O) = 21 k_7(N_2);$ $k_7(CO_2) = 5 k_7(N_2);$ $k_7(CO) = 2 k_7(N_2);$

$k_7(H_2) = 3.3 k_7(N_2)$

$k_{17}(H_2O) = 6 k_{17}(N_2);$ $k_{17}(H) = 2 k_{17}(N_2);$ $k_{17}(H_2) = 3 k_{17}(N_2)$

mine these activation energies. As we will show later in this paper, the model results agree best with experimental data when $k_{149} \simeq 0.77$ sec^{-1} and $k_{161} \simeq 23$ sec^{-1} at 1300 K. The relative dominance of Reaction 161 over Reaction 149 agrees with recent experimental and modeling results of Kiefer *et al.* (1982).

Hydrogen atom abstraction from propane occurs through radical attack on both primary and secondary sites. Reactions with H, O, and OH are generally most important, while abstraction by HO_2, CH_3, and other hydrocarbon radicals is usually less significant. Overall, the higher probability of abstraction of a secondary H atom is approximately balanced in C_3H_8 by the greater number of primary H atoms, so the total rates of primary and secondary H atom abstraction are nearly equal. For reactions with OH radicals

$$C_3H_8 + OH = iC_3H_7 + H_2O \qquad (110)$$

$$C_3H_8 + OH = nC_3H_7 + H_2O \qquad (111)$$
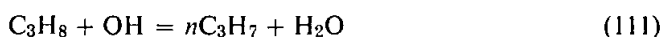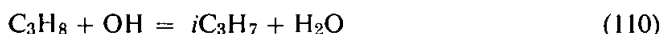
the rate expressions of Tully *et al.* (1983), based on a flash photolysis-resonance fluorescence technique and covering a temperature range from room temperature to nearly 700 K, were used. An expression for secondary H atom abstraction was determined by subtracting the rate of primary H atom abstraction in ethane (Reaction 50) from the experimentally determined total rate of reaction between propane and OH radicals. The ratio of secondary to total H atom abstraction, estimated in this manner, varies from 0.52 at 1000 K to 0.48 at 1500 K, so it was assumed that the same rate expression could be used for both k_{110} and k_{111}, half of the total rate measured by Tully *et al.* Subsequent computations of propane oxidation in the flow reactor led to slight modifications in these rates, with the final expressions given in Table 1. The non-Arrhenius ($T^{1.4}$) temperature dependence in these rates leads to a larger rate of reaction at the combustion temperatures included here ($1000 \rightarrow 1700$ K) than those based on lower temperature studies (see Warnatz, 1983a).

Abstraction by H atoms from alkane molecules has been studied by a number of authors. Some of the resulting rate expressions for Reactions 97 and 98

$$C_3H_8 + H = iC_3H_7 + H_2 \qquad (97)$$

$$C_3H_8 + H = nC_3H_7 + H_2 \qquad (98)$$
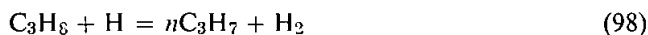
are summarized in Figure 1. During the course of the shock tube propane pyrolysis and oxidation modeling analysis described below, it was found that the computed results were very sensitive to the rates of Reactions 97 and 98, and that the high temperature rates must be larger than the linear extrapolations of the low temperature expressions. However, computed results for the flow reactor models at about 1100 K agreed best with experimental data when the rates of these reactions were smaller than the linear Arrhenius expression of Baldwin *et al.* (1977). Since substantial non-Arrhenius temperature dependence is observed for reactions of H atoms with both CH_4 and C_2H_6 (Clark and Dove, 1973), it was assumed that similar behavior could be anticipated for propane as well. Therefore a dependence of both k_{97} and k_{98} on T^2 was postulated. In addition, Hautman *et al.* (1981) concluded from propane pyrolysis studies in the flow reactor at $T \simeq 1100$ K that $E_{98} - E_{97} \simeq 2700$ cal/mole. The pre-exponential factors were finally adjusted to reproduce observed data on propane pyrolysis and oxidation in both shock tubes and the flow reactor, described
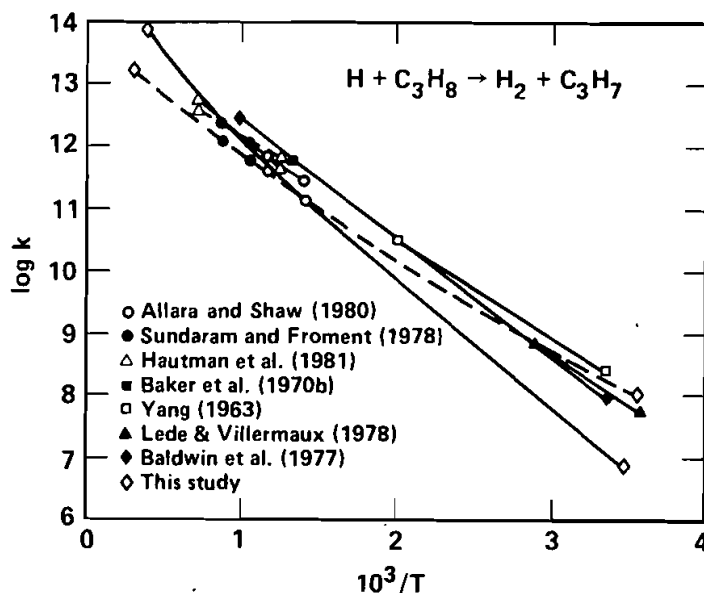
FIGURE 1   Reaction rate expressions for $H+C_3H_8=H_2+C_3H_7$. Dashed curves refer to production of iC_3H_7 radicals, solid curves to production of nC_3H_7 radicals or the sum of the two product channels.

below, arriving at the final expressions indicated in Table 1 and shown graphically in Figure 1.

Low temperature studies of H atom abstraction by O atoms (Walker, 1975; Huie and Herron, 1975) indicate that the rates of Reactions 108 and 109

$$C_3H_8 + O = iC_3H_7 + OH \tag{108}$$

$$C_3H_8 + O = nC_3H_7 + OH \tag{109}$$

are roughly comparable with those of reactions with H and OH. Therefore, because of the non-Arrhenius behavior of Reactions 97, 98, 110, and 111, it was assumed that Reactions 108 and 109 varied with T^2. The available experimental data were then fitted to this type of expression. The rates of the two product channels were assumed equal. None of the computed model results, regardless of the experimental regime, were sensitive enough to variations in the rates of Reactions 108 and 109 to provide further information on their rates or branching ratios. Under fuel-lean conditions most of the propane consumption occurs by means of reactions with OH radicals and under rich conditions with H atoms. Reactions 108 and 109 with O atoms were always less important than these other abstraction reactions.

Reactions between propane and other radical species are much less significant than those with H, O, and OH. For reactions with HO_2

$$C_3H_8 + HO_2 = iC_3H_7 + H_2O_2 \tag{112}$$

$$C_3H_8 + HO_2 = nC_3H_7 + H_2O_2 \qquad (113)$$
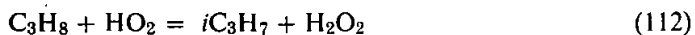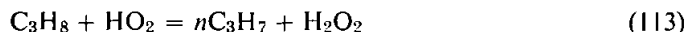
rate expressions were estimated by assuming an activation of 18 kcal/mole (the same as for Reaction 37 between CH_4 and HO_2, and close to the 19.36 kcal/mole for the analogous Reaction 85 with methanol), together with a pre-exponential of 5×10^{12} cm^3/mole-sec. This expression, used for both k_{112} and k_{113}, is very close to that recommended by Baldwin *et al.* (1977) and by Warnatz (1983a). For Reactions 95 and 96 with methyl radicals

$$C_3H_8 + CH_3 = iC_3H_7 + CH_4 \qquad (95)$$

$$C_3H_8 + CH_3 = nC_3H_7 + CH_4 \qquad (96)$$
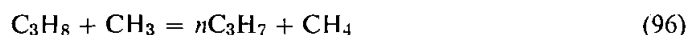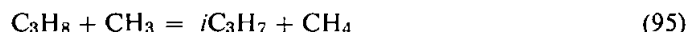
most of the available rate data agree very well over the temperature range of interest in this study, and the expressions in Table I are those determined by Hautman *et al.* (1981), assuming that the observed total rate of reaction is evenly divided between Reactions 95 and 96. Reactions 104–107 and Reactions 135 and 136 between propane and additional hydrocarbon radicals have also been adopted from the propane pyrolysis study of Hautman *et al.*

Reactions of propyl radicals are a very important part of the overall reaction mechanism. In the present mechanism, both isomeric forms can react with O_2 molecules or decompose thermally. Warnatz (1981, 1983b) has shown that in laminar propane–air flames, the thermal decomposition reactions are far more important than reactions with O_2. Most of the present modeling results presented below concur with that view, except for the very fuel-lean, low temperature flow reactor case. The rates of Reactions 115 and 116

$$iC_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (115)$$

$$nC_3H_7 + O_2 = C_3H_6 + HO_2 \qquad (116)$$
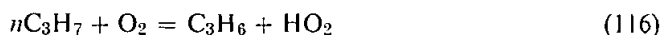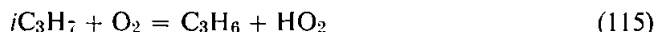
have been set equal to the analogous Reaction 53 for the ethyl radical. The activation energy of Reaction 115 should probably be slightly higher than that of Reaction 116, but there is little information available on these reactions, and the estimated rate expressions are probably satisfactory.

The thermal decomposition reactions of the propyl radicals include

$$iC_3H_7 = H + C_3H_6 \qquad (99)$$

$$iC_3H_7 = CH_3 + C_2H_4 \qquad (100)$$

$$nC_3H_7 = CH_3 + C_2H_4 \qquad (101)$$

$$nC_3H_7 = H + C_3H_6 \qquad (102)$$

Considerable attention has been directed towards these reactions, which are responsible for many of the central features of propane oxidation and pyrolysis. Use of the "one bond removed rule" (Dryer and Glassman, 1979) indicates that the rate of Reaction 100 is very small. It is completely neglected (as unimportant) by most studies (Edelson and Allara, 1980; Allara and Shaw, 1980; Sundaram and Froment,

1978; Bakh *et al.*, 1974), while others (Papic and Laidler, 1971; Jackson and McNesby, 1962; Falconer *et al.*, 1963) conclude that more than 90 percent of the iC_3H_7 radicals decompose by Reaction 99. The rate expressions for k_{99} and k_{100} in Table I have been taken from the paper of Kerr and Trotman-Dickenson (1959) and used by Hautman *et al.* (1981). Therefore, it can be assumed that the decomposition of iso-propyl radicals essentially produces only H atoms and C_3H_6. In contrast, the decomposition Reaction 101 of *n*-propyl radicals producing methyl radicals and ethylene is generally dominant over Reaction 102 which is considerably slower, although not nearly as slow as Reaction 100. Rates of Reactions 101 and 102 were adopted from the results of Jackson and McNesby (1962), used also by Hautman *et al.* The rate of Reaction 101 was subsequently increased by 20 percent to obtain better agreement between computed and experimental data in the flow reactor and shock tube simulations, resulting in the expression in Table I.

In both oxidation and pyrolysis of propane, modeling results indicate that it is crucial to describe accurately the relative rates of production of the two propyl radicals. Production of iso-propyl radicals has an overall effect of accelerating the oxidation of propane because the H atom produced by Reaction 99 can then react with O_2

$$H + O_2 = O + OH \qquad\qquad (1)$$

and provide chain branching. However, the products of the major decomposition reaction of *n*-propyl radicals, Reaction 101, are the relatively unreactive C_2H_4 and CH_3. In fact, because a significant fraction of the methyl radicals recombine through Reaction -47,

$$CH_3 + CH_3 = C_2H_6 \qquad\qquad (-47)$$

Reaction 101 actually leads to a considerable amount of chain termination. In pyrolysis regimes, the H atoms from Reaction 99 have a considerably larger rate of reaction with propane than do the methyl radicals from Reaction 101, so again the production of iC_3H_7 results in a larger overall rate of reaction than does the production of nC_3H_7 radicals.

Selection of appropriate elementary reactions, their products, and their rates was more difficult and ambiguous for propene than for propane. In the great majority of cases, rates and product distributions for reactions between O or OH radicals and propene are known only at relatively low temperatures (*i.e.* 250–500 K). However, it is quite possible that product channels which are not accessible or important at these temperatures may become significant above 1000 K. In constructing the present reaction mechanism, the general approach has been to include a number of feasible product channels and examine the sensitivity of the computed results to the choice of product distribution.

Three possible reactions between C_3H_6 and O atoms have been included

$$C_3H_6 + O = C_2H_4 + CH_2O \qquad\qquad (114)$$

$$C_3H_6 + O = C_2H_5 + HCO \qquad\qquad (120)$$

$$C_3H_6 + O = CH_3 + CH_3CO \qquad\qquad (122)$$

Warnatz (1983b) includes only Reaction 122, while Cathonnet *et al.* (1981) considered only Reaction 120. Reaction 114 was postulated by analogy with Reaction 58.

$$C_2H_4 + O = CH_2O + CH_2 \tag{58}$$

The possibility of ethylene and formaldehyde as products was suggested by the mechanism of Cathonnet *et al.* which included these as decomposition products of C_3H_6O, which decomposes into a variety of unimolecular and fragmented species (Flowers, 1977). Perry (1983) ruled out an abstraction channel for temperatures as high as 820 K, and no such channel has been considered in the present mechanism. Perry also determined empirical fits to experimental data for the total rate of reaction between propene and oxygen atoms, using a laser photolysis-chemiluminescence technique, leading to the expression

$$k(C_3H_6 + O) = 2.05 \times 10^5 \, T^{2.56} \exp(+1130/RT) \, cm^3/mole\text{-}sec.$$

Rate expressions for Reactions 120 and 122 were initially taken from Cathonnet *et al.* and from Warnatz, respectively, and Reaction 114 was assumed to have the same rate as Reaction 58. Subsequently, these expressions were scaled upwards from their original values by a factor of about two in order to agree with Perry's expression at 1000 K. However, reactions between propene and oxygen atoms provide a relatively minor fraction of the propene consumption in all of the propane and propene oxidation cases examined by the present model, and no further conclusions could be reached about the relative or absolute rates of these reactions. Additional study is needed to determine the rates and product distributions as functions of temperature. This conclusion is reinforced by the fact that, in his recent review of rate coefficients in the C/H/O system, Warnatz (1983a) considers only the non-specific reaction

$$C_3H_6 + O = products.$$
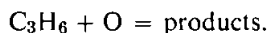
A similar procedure was followed for reactions between propene and OH

$$C_3H_6 + OH = C_2H_5 + CH_2O \tag{119}$$

$$C_3H_6 + OH = CH_3 + CH_3CHO \tag{121}$$

$$C_3H_6 + OH = C_3H_5 + H_2O \tag{134}$$
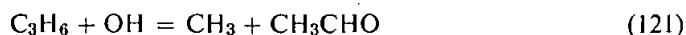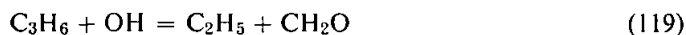
Warnatz (1983b) includes only Reaction 121, but with a rate of 10^{13} $cm^3/mole\text{-}sec$, close to the sum $k_{119} + k_{121} + k_{134}$ from Table I. Cathonnet *et al.* (1981) instead include Reactions 119 and 134, both with the same rate of 8×10^{12} $cm^3/mole\text{-}sec$. Like many other reactions between radical species and unsaturated hydrocarbons, at low temperatures this is an addition reaction followed by a rearrangement and decomposition, while at temperatures above about 800 K the abstraction channel is likely to dominate. All of the experimental data available for these reactions (see Warnatz, 1983a) consider temperatures below 500 K, and a great deal of work is needed to improve current understanding of this reaction, which is probably a major path for propene oxidation under most combustion conditions. The modeling analysis described below provided a value of k_{121} at about 1100 K and an estimate of the ratio k_{119}/k_{134} above 1000 K.

Reactions between propene and H atoms include both addition and abstraction

$$C_3H_6 + H = iC_3H_7 \qquad (-99)$$

$$C_3H_6 + H = nC_3H_7 \qquad (-102)$$

$$C_3H_6 + H = C_3H_5 + H_2 \qquad (131)$$

All three reactions have been studied extensively for propene pyrolysis. Above 1000 K, both of the addition reactions have very nearly the same rate, although some studies (Allara and Edelson, 1975; Sundaram and Froment, 1978; Warnatz, 1983a) indicate that the activation energy for Reaction −99 is 1–2 kcal/mole smaller than for Reaction −102. Recalling the discussion above about the importance of distinguishing between the forward Reactions 99 and 101 and their different effects on the overall rate of reaction, Reaction −102 has a particularly large influence on computed results. This is caused by the fact that the sequence

$$C_3H_6 + H = nC_3H_7 \qquad (-102)$$

$$nC_3H_7 = CH_3 + C_2H_4 \qquad (101)$$

has a strong inhibiting influence, and the sequence

$$iC_3H_7 = H + C_3H_6 \qquad (99)$$

$$C_3H_6 + H = nC_3H_7 \qquad (-102)$$

is equivalent to an isomerization reaction. Since nC_3H_7 does not produce $H + C_3H_6$ in appreciable quantities through Reaction 102, the reverse isomerization from nC_3H_7 to iC_3H_7 through $H + C_3H_6$ is not important.

The abstraction Reaction 131 has been shown (Burcat, 1975; Amano and Uchiyama, 1963, 1964; Edelson and Allara, 1980; Szwarc, 1949; Allara and Edelson, 1975; Sundaram and Froment, 1978; Yano, 1977) to be important in propene pyrolysis. Alternatively, Laidler and Wojciechowski (1960) treated the formation of allyl radicals through a sequence

$$C_3H_6 + H = nC_3H_7$$
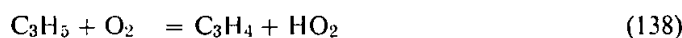$$nC_3H_7 = C_3H_5 + H_2$$
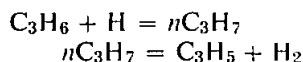
but the second reaction has been rejected in the present work as negligible relative to the rate of Reaction 101. In this study the rate expression of Amano and Uchiyama (1963) was adopted initially, then reduced by a factor of two after comparison between computed and experimental results.

Additional H atom abstraction reactions from propene have been included with Reactions 132 and 133

$$C_3H_6 + CH_3 = C_3H_5 + CH_4 \qquad (132)$$

$$C_3H_6 + C_2H_5 = C_3H_5 + C_2H_6 \qquad (133)$$
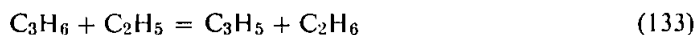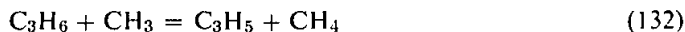
but these are generally much less important than Reaction 131.

Several paths for allyl radical consumption are included

$$C_3H_5 = C_3H_4 + H \qquad (137)$$

$$C_3H_5 + O_2 = C_3H_4 + HO_2 \qquad (138)$$

$$C_3H_5 + CH_3 = {}_1C_4H_8 \qquad (-139)$$

$$C_3H_5 + H = C_3H_4 + H_2 \qquad (162)$$

$$C_3H_5 + CH_3 = C_3H_4 + CH_4 \qquad (163)$$

In contrast with many other hydrocarbon radicals (Westbrook and Dryer, 1983), the allyl radical is unusually stable and Reaction 137 has a prohibitively high activation energy. As a result of this stability, it is likely that allyl-radical reactions such as Reactions 162 and 163 will actually dominate the consumption of allyl radicals. However, very little high temperature information on such reactions is available. A fairly high percentage of allyl radicals must produce C_3H_4 since both allene and propyne are produced in propene pyrolysis (Burcat, 1975). Reaction 138 has been proposed in the present mechanism to model the conversion of allyl to C_3H_4 under oxidizing conditions, although it is somewhat unlikely that this path represents an elementary reaction of real significance. Further information is needed to establish the actual elementary reactions responsible for this conversion which are likely to include the steps

$$C_3H_5 + O = C_3H_4 + OH$$

$$C_3H_5 + OH = C_3H_4 + H_2O$$
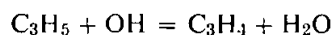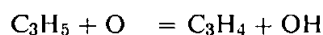
as well as addition paths. It is also possible that some C_3H_4 formation does not proceed directly from allyl radicals, but no such alternative formation path was considered.

Another path for allyl radical consumption consists of recombination reactions such as Reaction -139, included to reproduce observed butene concentrations in flow reactor experiments. This reaction and Reaction -140

$$C_2H_3 + C_2H_5 = {}_1C_4H_8 \qquad (-140)$$

were initially assigned rates equal to that of methyl recombination

$$CH_3 + CH_3 = C_2H_6 \qquad (-47)$$
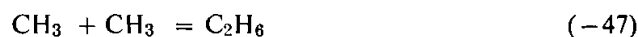
but k_{-139} was subsequently increased by 50 percent to reproduce the butene measurements (described further below), resulting in a rate expression in good agreement with that of Allara and Shaw (1980), but much greater than that of Sundaram and Froment (1978).

Finally, the consumption of ${}_1C_4H_8$ produced by Reaction -139 and C_3H_4 (no distinction has been made in the mechanism between allene and propyne) has been estimated by Reactions 141–148. Product distributions for all of these reactions have

B

not been established at temperatures above 1000 K, and future modeling and experimental analysis of these systems is planned. Computed results for the problems considered here were insensitive to variations in the rates of these reactions, so no further mechanism refinement was possible in this area.

In addition to the mechanism development required to describe the combustion of propane and propene, two improvements to the C_2 mechanism have been made. Reaction 68

$$C_2H_2 + OH = CH_2CO + H \tag{68}$$

has been changed to reflect recent work (Miller et al., 1983; Levy et al., 1983; Warnatz et al., 1983) indicating that ketene and H atoms are the products rather than CH_3 and CO as previously assumed. Also now included is an alternative product channel for reactions between acetylene and O atoms

$$C_2H_2 + O = HCCO + H. \tag{150}$$

Rates for these reactions, as well as the subsequent reactions of ketene and ketyl radicals, have been taken largely from Miller et al. and from Warnatz.

Another modification to the previously existing C_2 mechanism involves replacing a low temperature rate expression (Greiner, 1970) for Reaction 50

$$C_2H_6 + OH = C_2H_5 + H_2O \tag{50}$$

by a more recent value reported by Tully et al. (1983). Extension of the experimental rate data to 800 K indicates that, like other reactions between OH and alkane molecules, k_{50} includes some non-Arrhenius curvature, so that use of the Greiner expression above 1000 K underestimates the value of k_{50}.

MECHANISM EVALUATION

The reaction mechanism was tested and refined by comparisons between computed results and experimental data from two distinctly different types of conditions, the turbulent flow reactor and the shock tube. The ranges of temperature, pressure, and equivalence ratio covered in these experiments are sufficiently wide to ensure that the resulting mechanism would be applicable to many practical combustion environments.

Propane Oxidation in the Turbulent Flow Reactor

The experimental data used in this study were obtained by Hautman (1980), using the Princeton University turbulent flow reactor which has provided data for many earlier modeling studies. In these experiments, dilute mixtures of propane and oxygen in a nitrogen carrier gas react in a cylindrical flow system. Species concentrations and temperature are measured as functions of axial distance along the centerline of the reactor duct. Further details on the experimental apparatus and measurement techniques are available from Dryer (1972) and Hautman (1980). Three sets of data were used in the comparisons with the computed results, one of which was nearly stoichiometric, one very rich and the other very lean. The initial conditions

TABLE II

ϕ	$[C_3H_8]_0$ (moles/cm^3)	$[O_2]_0$ (moles/cm^3)	Inlet velocity (cm/sec)	T_0 (K)
0.066	3.17×10^{-8}	2.40×10^{-6}	1020	1000
0.98	3.11×10^{-8}	1.58×10^{-7}	861	1131
1.59	5.32×10^{-8}	1.67×10^{-7}	917	1148

in these experiments are summarized in Table II, where ϕ is the equivalence ratio and the other quantities describe conditions at the flow reactor inlet.

Among the species detected were C_3H_8, C_3H_6, H_2, C_2H_4, CO, CO_2, CH_4, C_2H_6, CH_3CHO, and C_4H_8, although these last two were not observed in all three sets of data. Measured data for each case are indicated by the open symbols in Figures 2–4.

The computed models for each case used the initial conditions given in Table II. In each computation, an appreciable amount of reaction takes place in the mixing part of the flow reactor duct, prior to the location at which the first measurements are taken. Another feature in every case is the rapid rise in temperature and a sharp maximum in the CO concentration occurring immediately following the disappearance of the propane fuel. In order to compare the computed and experimentally determined species and temperature profiles, the location of this CO maximum was chosen as a spatial reference point. The computed species concentrations and temperatures for the three cases are shown as the solid curves in Figures 2–4. The general agreement is good, with the trends being very similar in all three models. As the propane fuel is consumed, a sequence of product species forms. The order in which they are produced corresponds with the spatial locations at which they reach their peak concentrations. The earliest major intermediate is propene, followed by ethylene, and then by methane, carbon monoxide and hydrogen. The consumption of these last intermediates and the majority of the temperature increase occur subsequent to the final disappearance of the fuel. From Figures 2 and 4 it appears that the numerical model predicts a somewhat more abrupt end to the fuel consumption phase than seen from the experimental data, resulting in a more rapid oxidation of CO and H_2 and a steeper temperature rise in the computed models. Concentrations of the major intermediate species are very close to the experimental data for all three models and the predicted methane concentration is about 25 percent smaller than the observed data.

It is evident from the propane concentration profiles that the model slightly overestimates the rate of fuel consumption in the lean case and underestimates its rate in the rich case. For the stoichiometric model both trends can be observed. The length of the reactor duct over which propane is consumed agrees well with the experimental data, but the computed profile is basically a straight line while the experimental results are somewhat curved. The computed results and the rate expressions in Table I therefore represent a compromise, with the best overall agreement for all three cases using a single reaction mechanism.

The dominant reactions for propane consumption vary with equivalence ratio. In the lean model, most of the fuel consumption occurs by Reactions 110 and 111 with OH radicals, while Reactions 97 and 98 with H atoms are most important in the rich case. Both pairs of reactions are important for the stoichiometric model. Computed results are quite sensitive to variations in these rates of propane consumption because
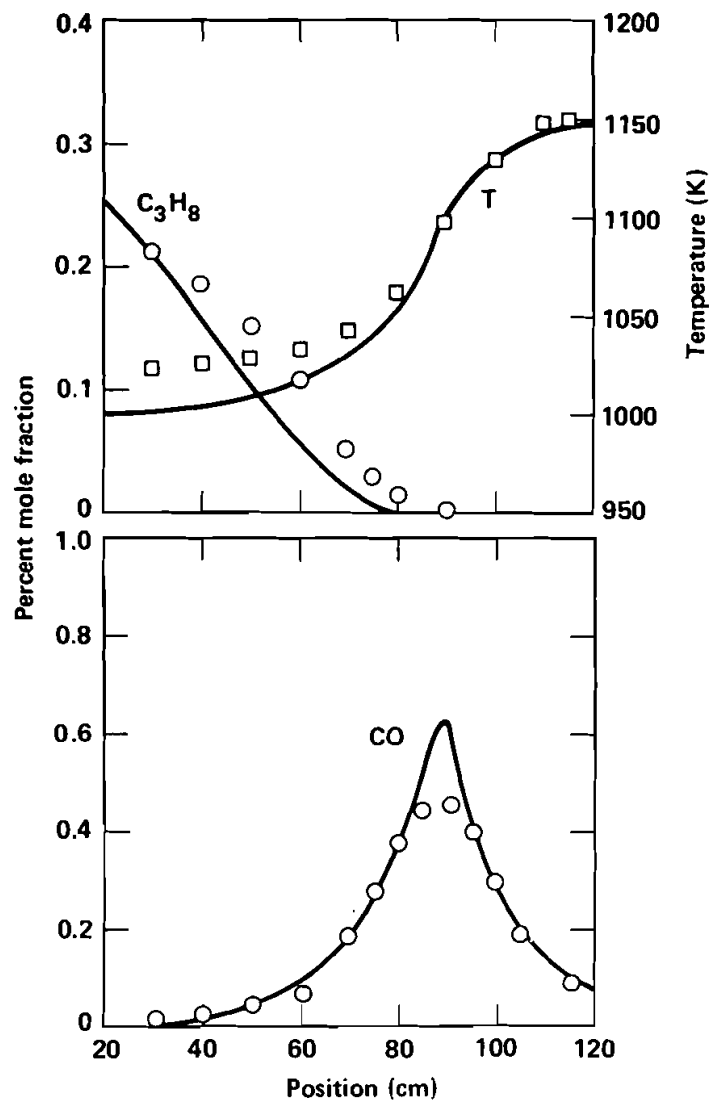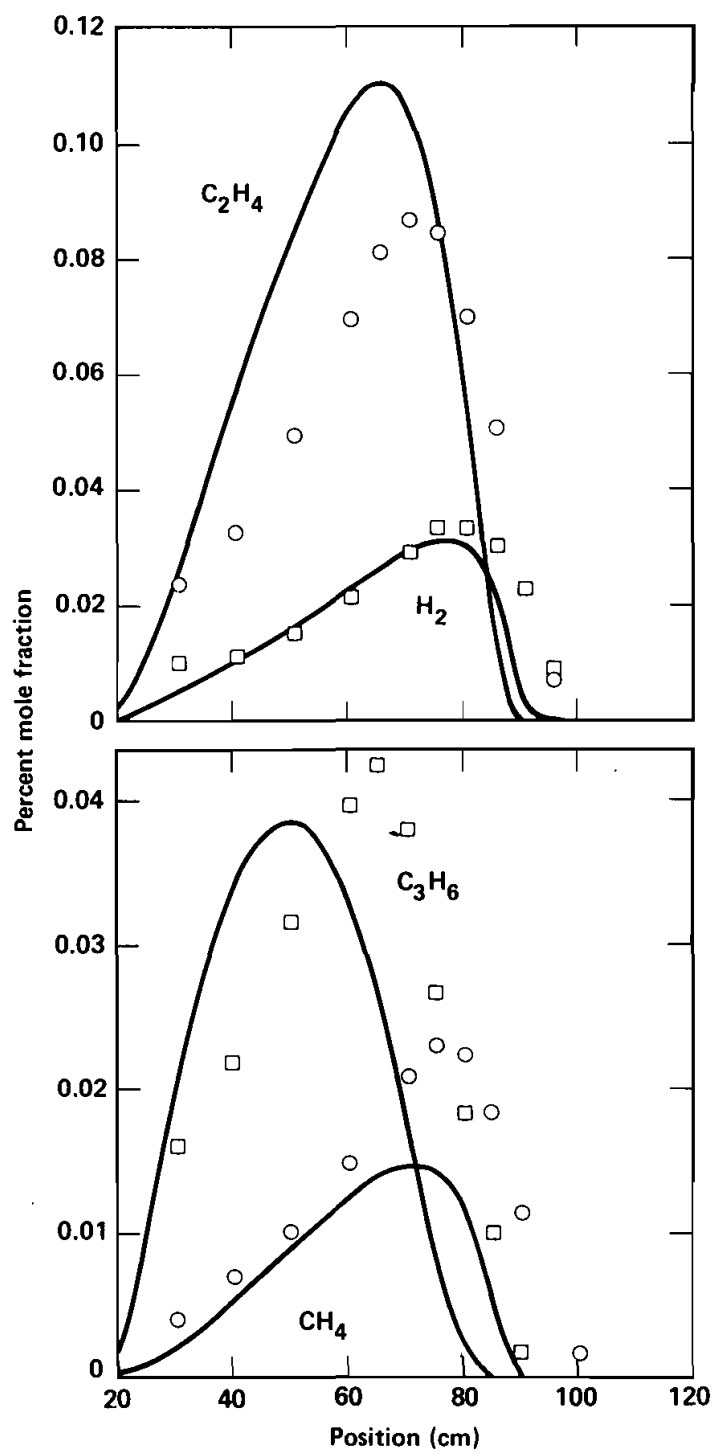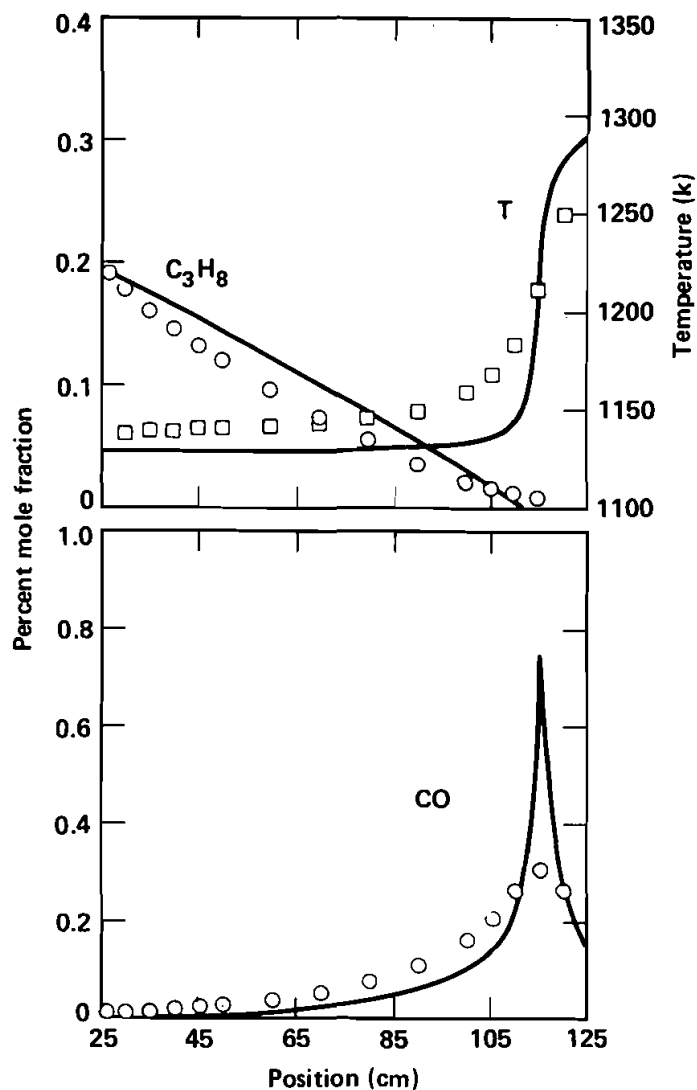
FIGURE 2a   Temperature and C_3H_8 and CO concentration profiles for lean flow reactor case. Symbols represent experimental data, curves are computed results, plotted as functions of axial distance from the inlet end of the flow reactor.

H atoms which do not react with C_3H_8 can instead react with O_2

$$H + O_2 = O + OH \tag{1}$$

and provide chain branching. Variations of a factor of ± 50 percent in the combined rates of $C_3H_8 + OH$ in the lean and stoichiometric models, and of $C_3H_8 + H$ in the rich and stoichiometric models, produced significantly poorer agreement between

FIGURE 3a   Temperature and C_3H_8 and CO concentration profiles for stoichiometric flow reactor case. Symbols represent experimental data, curves are computed results, plotted as functions of axial distance from the inlet end of the flow reactor.
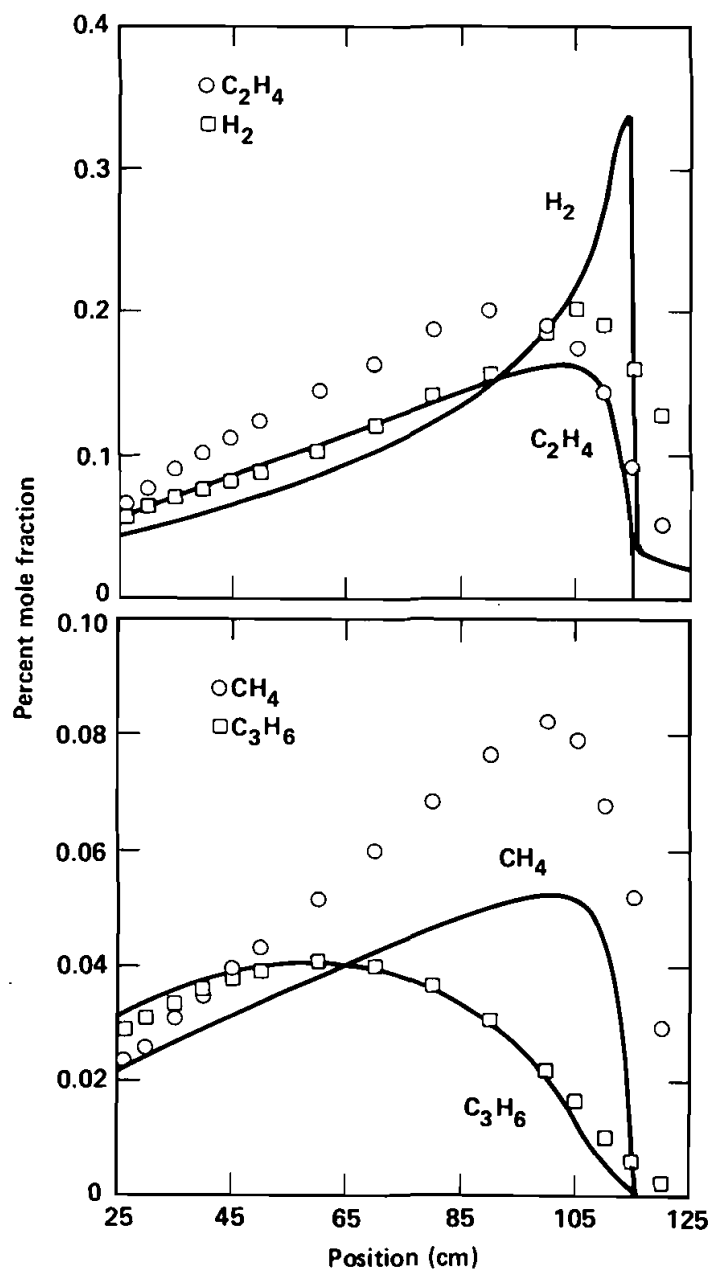
FIGURE 2b   Intermediate species concentration profiles for lean flow reactor case. Symbols represent experimental data, curves are computed results, plotted as functions of axial distance from the inlet end of the flow reactor.

FIGURE 3b   Intermediate species concentration profiles for stoichiometric flow reactor case. Symbols represent experimental data, curves are computed results, plotted as functions of axial distance from the inlet end of the flow reactor.
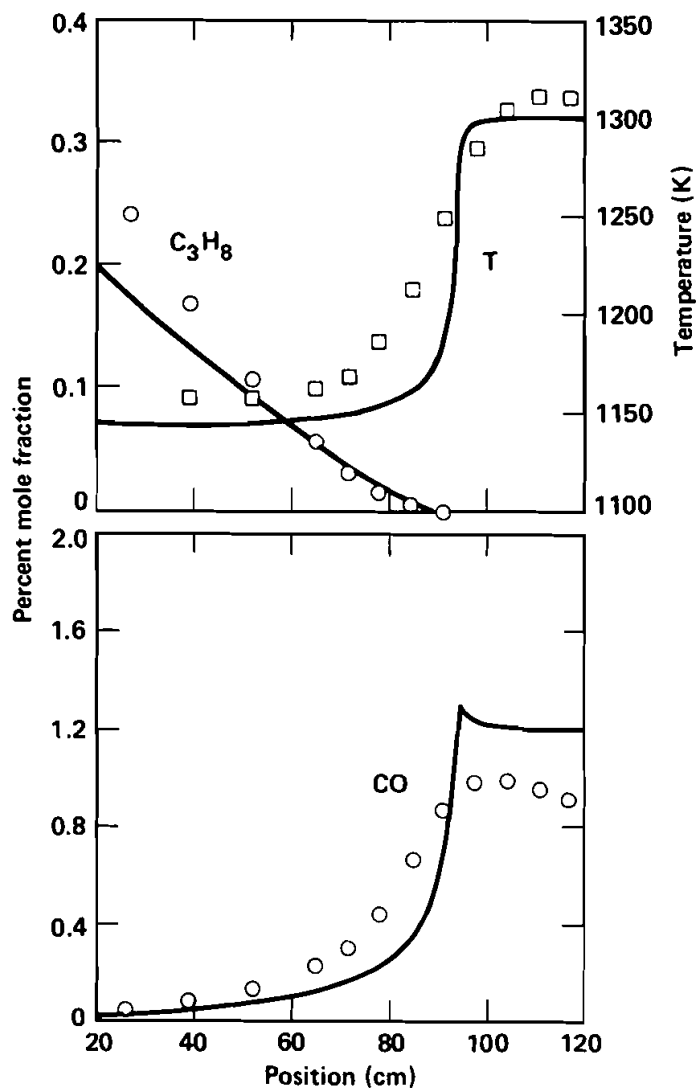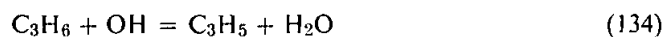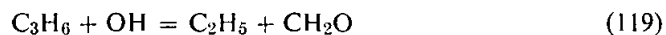
FIGURE 4a   Temperature and C_3H_8 and CO concentration profiles for rich flow reactor case. Symbols represent experimental data, curves are computed results, plotted as functions of axial distance from the inlet end of the flow reactor.

computed and experimental species and temperature profiles. Similar trends but with lower sensitivity were observed for major reactions of propene, with Reactions 119 and 134 most important in the lean case

$$C_3H_6 + OH = C_2H_5 + CH_2O \tag{119}$$

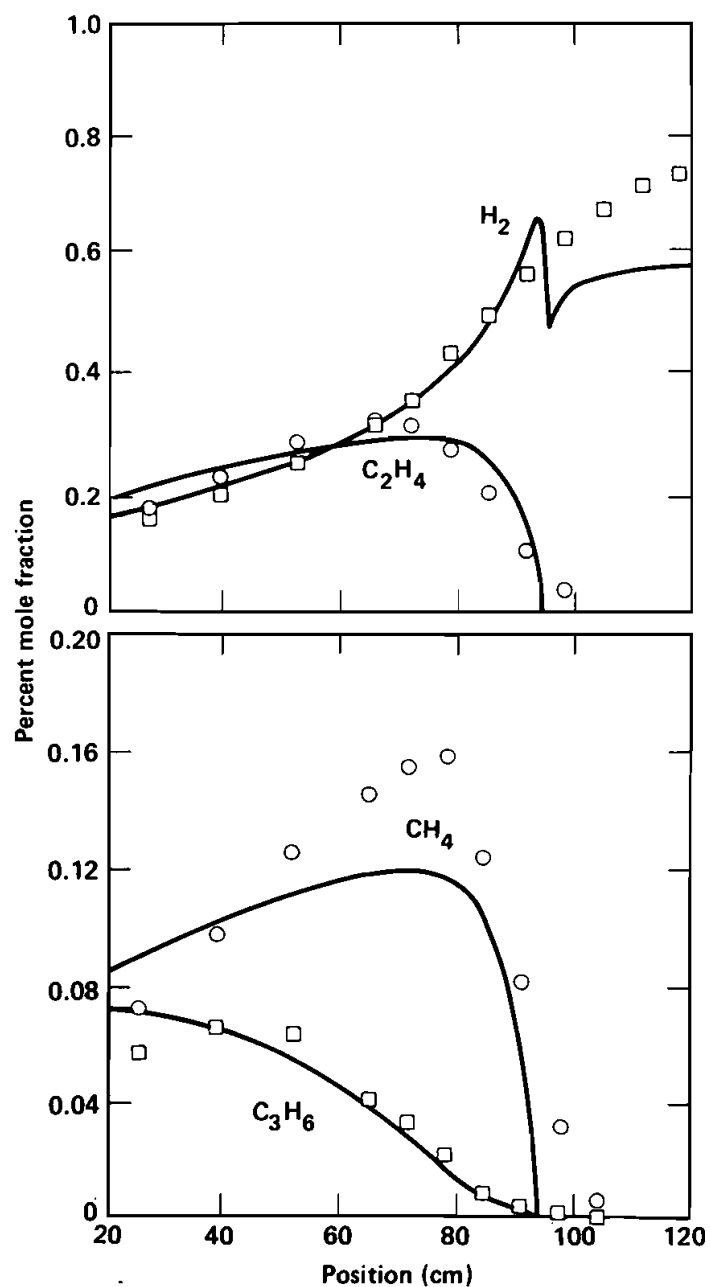$$C_3H_6 + OH = C_3H_5 + H_2O \tag{134}$$

FIGURE 4b Intermediate species concentration profiles for rich flow reactor case. Symbols represent experimental data, curves are computed results, plotted as functions of axial distance from the inlet end of the flow reactor.

$$C_3H_6 + \quad H = C_3H_5 + H_2 \qquad\qquad (131)$$

and Reaction 131 dominant for the rich case.

As discussed earlier, most of the propyl radical consumption occurs by thermal decomposition Reactions 99 and 101, so the relative rates of iC_3H_7 and nC_3H_7 formation from propane are very important. Only in the leanest case does Reaction 115

$$iC_3H_7 + O_2 = C_3H_6 + HO_2 \qquad\qquad (115)$$
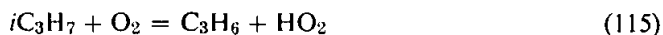
contribute as much as 25 percent of the consumption rate of iC_3H_7 radicals, while it is negligible in all of the other cases.

Consumption of allyl radicals also varies with equivalence ratio. In the rich model the principal path is the formation of butene, with Reaction 138 with O_2 being somewhat important. In the lean case, however, Reaction 138 is dominant.

$$C_3H_5 + O_2 \quad = C_3H_4 + HO_2 \qquad\qquad (138)$$

$$C_3H_5 + CH_3 = {}_1C_4H_8. \qquad\qquad (139)$$
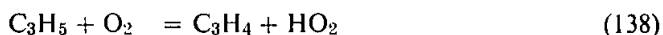
The overall rate of propane oxidation is quite sensitive to the ratio of the rates of Reactions 138 and 139. Reaction 139 provides chain termination, while Reaction 138 slightly accelerates the overall reaction rate. In the numerical simulations of the flow reactor experiments, k_{139} was determined by requiring that the observed concentration of C_4H_8 be properly reproduced. The rate expression determined by this process (see Table I) is 50 percent larger than the rate of the recombination Reaction -47

$$CH_3 + CH_3 = C_2H_6. \qquad\qquad (-47)$$
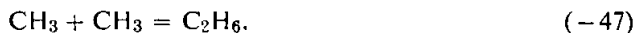
The rate of Reaction 138 was then varied to reproduce the correct length of the reaction zone in the three flow reactor models. At 1100 K, k_{138} is slightly less than k_{63}

$$C_2H_3 + O_2 \quad = C_2H_2 + HO_2. \qquad\qquad (63)$$
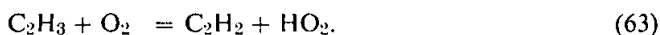
In a similar manner, the rate of Reaction 121

$$C_3H_6 + OH = CH_3 + CH_3CHO \qquad\qquad (121)$$
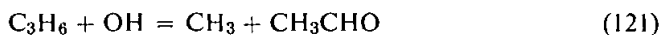
was determined by reproducing the observed levels of acetaldehyde in the fuel-lean case (the only case in which acetaldehyde had been detected experimentally). Although Reaction 121 is more exothermic than Reactions 119 and 134 with the same reactants, its rate at 1100 K was found to be considerably smaller than either k_{119} or k_{134}.

The flow reactor simulations were found to be relatively insensitive to the details of the reaction paths consuming C_4H_8, C_3H_4, and CH_3CHO. As a result, these model calculations can provide little information on the rates and product distributions of reactions between these intermediates and radical species O and OH.

Shock Tube Oxidation of Propane

Propane oxidation in reflected shock waves was studied experimentally by Burcat et al. (1971a, 1971b) over a temperature range of 1250–1700 K, at equivalence ratios

TABLE III

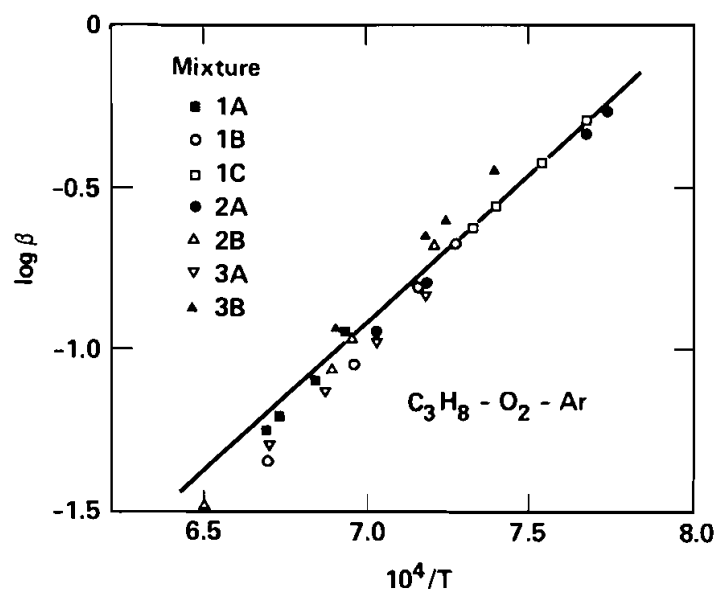| Mixture	%C$_3$H$_8$	%O$_2$	ϕ
1A	1.6	8.0	1
1B	0.48	2.4	1
1C	1.6	8.0	1
1D	3.85	19.23	1
2A	0.8	8.0	0.5
2B	0.84	2.1	2
3A	0.41	4.1	0.5
3B	1.6	4.0	2

FIGURE 5   Correlation functions for shock tube ignition of C$_3$H$_8$-O$_2$-Ar mixtures. Solid line is the overall correlation from Burcat *et al.* (1971b), symbols are model computations for specific mixtures given in Table III.

between 0.125 and 2.0, and pressures between 2 and 15 atmospheres. Experimental ignition delays from both studies were used to test the present reaction mechanism.

Eight separate propane–oxygen–argon mixtures were taken from the experimental data of Burcat *et al.* (1971b), with the initial compositions shown in Table III.

The initial temperatures were varied from 1250 to 1500 K. In each computation the ignition delay time τ was defined as the time corresponding to the maximum rate of reaction between CO and O atoms. Other realistic definitions of τ, such as the time of maximum rate of pressure or temperature rise, give nearly identical results. From the experimental results, Burcat *et al.* found that τ could be approximated in terms of the initial temperature T and reactant concentrations (in moles/cm^3) by

$$\tau = 4.4 \times 10^{-14} \exp(21240/T_0)[Ar]^0[C_3H_8]^{0.57}[O_2]^{-1.22} \text{ sec}$$

From the computed ignition delay time and the initial temperature and reactant concentrations, model values of the correlation function β

$$\beta = \tau[O_2]^{1.22}[C_3H_8]^{-0.57} \ \mu s \ (mole/cm^3)^{0.65}$$

were calculated, and the results are summarized in Figure 5. The solid line represents the overall correlation function determined by Burcat *et al.*, while the individual symbols represent computed values of β. The general agreement is very good, although the computed results at the highest temperatures appear to fall slightly below the experimental correlation line.

Many of the same general trends were found in these modeling results as in the flow reactor oxidation simulations. For propane and propene consumption, reactions with H atoms dominated in rich conditions, while reactions with OH were most important in lean mixtures. The ratio of production rates of the two propyl radicals was again of primary importance, due to the differences in their effects on subsequent radical production rates. It was also found that the rates of recombination reactions between H atoms and C_3H_6 were important, since the sequence

$$H + C_3H_6 = nC_3H_7 \qquad\qquad\qquad (-102)$$

$$nC_3H_7 = CH_3 + C_2H_4 \qquad\qquad\qquad (101)$$

results in a significant amount of chain termination. In these relatively low temperature shocks, formation of $_1C_4H_8$ by Reaction 139 is still important.

In addition to these primarily dilute systems, the model was used to simulate the shock tube propane ignition results of Burcat *et al.* (1971a) in which stoichiometric mixtures of 3.22% C_3H_8–16.1% O_2–80.68% Ar were studied. Together with other alkane fuel ignition experiments, these mixtures had been selected because they represented a reasonable approximation to the reactant proportions of these fuels in air. The present reaction mechanism accurately reproduced the experimentally observed ignition delay times to within ± 5 percent over a temperature range of 1240–1690 K, at initial pressures between 7 and 15 atmospheres. This series of numerical simulations is an especially important step towards the modeling of induction times in propane–air and propane–oxygen detonations (Westbrook *et al.*, 1983b), since the initial temperatures, pressures, and reactant concentrations in these experiments encompass those which occur behind the incident shock wave associated with a detonation.

Propane Pyrolysis

Propane decomposition has been studied experimentally in tubular flow reactors (Hautman *et al.*, 1980, 1981; Illes, 1971; Camilleri *et al.*, 1975; Herriott *et al.*, 1972), static vessels (Laidler *et al.*, 1962; Leathard and Purnell, 1968), and shock tubes (Lifshitz *et al.*, 1973, 1975; Chiang and Skinner, 1981; Koike and Gardiner, 1980; Simmie *et al.*, 1982; Al-Alami and Kiefer, 1983). The propane pyrolysis submechanism in Table I is very similar to that developed by Hautman *et al.*, and the present model reproduces experimental data from the flow reactor satisfactorily.

Shock tube data of Chiang and Skinner were selected for particular attention. In these experiments, dilute mixtures of propane in argon were pyrolysed behind reflected shock waves at temperatures of 1200–1450 K and pressures of 2–3 atmospheres.

Time dependent concentrations of H atoms were measured by resonance absorption spectroscopy. The overall reaction is described by a fairly limited mechanism, including

$$C_3H_8 = CH_3 + C_2H_5 \tag{94}$$

$$C_2H_5 + M = C_2H_4 + H + M \tag{52}$$

$$C_3H_8 + H = iC_3H_8 + H_2 \tag{97}$$

$$C_3H_8 + H = nC_3H_8 + H_2 \tag{98}$$

$$iC_3H_7 = C_3H_6 + H \tag{99}$$

Reaction 52 can be considered to be essentially instantaneous, so the initiation consists effectively of

$$C_3H_8 = CH_3 + C_2H_4 + H.$$
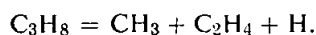
In each pyrolysis experiment, the H atom concentration rises initially as a result of Reactions 94 and 52, and the initial slope of [H] vs. time was used in the experiments to evaluate k_{94}. Eventually, consumption by Reactions 97 and 98 results in a decreased rate of growth of H atom levels, until a quasi-equilibrium is established where the net rate of H atom production is considerably less than the rate of Reaction 94. Computed H atom profiles for three different cases are shown in Figure 6, all consisting initially of 5 ppm C_3H_8 in argon. Also shown are the experimentally measured H atom concentrations near the end of each run. At 160 μs for Case (a) at 1422 K, H atom production from Reactions 52 and 99 is still more than four times larger than the rate of H atom consumption. In Case (c) at 1298 K, however, production of H atoms at 1600 μs is nearly balanced by consumption, with the ratio of H atom production to consumption being approximately 3:2. Of the thirteen separate cases reported by Chiang and Skinner for C_3H_8 pyrolysis, about one-third give H atom concentrations during the initial growth phase, another third give data after the quasi-equilibrium is established, and the remainder fall in between these extremes. In the modeling results, the initial slopes for H atom production computed from k_{94} in Table I agree very well with the experimental values. In addition, calculated H atom levels at the end of each run agree closely with the experimental data, as illustrated for the three cases in Figure 6.

Computed quasi-equilibrium H atom levels, in those cases where residence times were sufficiently long, were found to depend on the sum of the reaction rates between propane and H atoms, $k_{97} + k_{98}$. Using either k_{94} from Table I or the nearly equivalent rate expression from Chiang and Skinner, the modeling results do not provide independent determinations of k_{97} and k_{98}, but their sum over the range 1200–1450 K is accurately given by the expressions in Table I, probably to within a factor of two. When both rates are doubled, computed quasi-equilibrium H atom levels are too small by more than 50 per cent, while a decrease in k_{97} and k_{98} of a factor of two results in noticeable errors in the flow reactor oxidation simulations already described. Reaction 52 is so rapid that the computed H atom histories were completely insensitive to its rate. In all the cases residence times were short enough that secondary reactions of C_2H_4 and C_3H_6 played essentially no part.
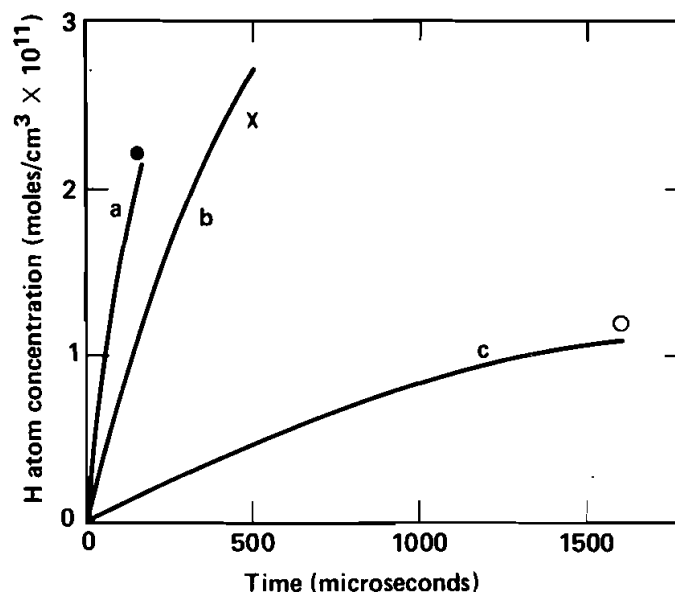
FIGURE 6   Variation in H atom concentrations with time, computed by the model. Initial conditions in each case are 5 ppm propane in argon. Temperatures are (a) 1422 K, (b) 1382 K, (c) 1298 K. Experimental data from Chiang and Skinner (1981) indicated by large symbols.

The final expression for k_{94} in Table I is about twice that determined by Chiang and Skinner from their own modeling analysis. Simmie *et al.* (1982) compared their value of $k_{94} = 190$ s^{-1} at 1333 K with $k_{94} = 110$ s^{-1} from Chiang and Skinner, and $k_{94} = 110$ s^{-1} from Lifshitz and Frenklach (1975). At the same temperature, the present mechanism gives $k_{94} = 208$ s^{-1}, very close to the value determined by Simmie *et al.* This is also within a factor of two of the expression of Al-Alami and Kiefer (1983), extrapolated slightly to 1333 K since their study did not extend below 1400 K. The shock tube experiments of Al-Alami and Kiefer were carried out at higher temperatures and considerably lower densities than those of Chiang and Skinner or Simmie *et al.* As emphasized by each of these papers, such differences will affect the amount of falloff to be expected in k_{94}, and different propane concentrations and diluent species will also produce noticeable effects. Furthermore, in each of these studies the determination of k_{94} depends in part on the rates of the other pyrolysis reactions, particularly Reactions 97 and 98, which are different in each model. Considering all of these factors, the agreement between the expression for k_{94} in Table I and other available expressions is quite acceptable.

Propene Pyrolysis .

The shock tube pyrolysis of propene has been studied by a number of authors. For the present model, the high temperature study of Burcat (1975) was chosen for modeling analysis because the initial and final conditions for a large number of individual shock experiments were directly available. In the experiments, propene was highly diluted by argon (either 99.6 or 98.4% Ar), and its pyrolysis was observed

in a single pulse shock tube over a temperature range 1160–1700 K. The products observed after the dwell time of approximately 800 μsec were C_3H_6, H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_4. Both allene and propyne were observed.

As discussed earlier, the two initiation reactions are

$$C_3H_6 = C_3H_5 + H \tag{149}$$

$$C_3H_6 = C_2H_3 + CH_3. \tag{161}$$

Since vinyl radicals rapidly dissociate into acetylene and H atoms, both paths quickly provide H atoms to the radical pool. However, unless Reaction 161 is the dominant initiation step, predicted acetylene concentrations are much lower than those observed experimentally.

The overall trends in the experiments were reasonably well reproduced by the model. The rate of propene consumption and the rates of production of pyrolysis products follow an overall Arrhenius behavior until most of the fuel has been destroyed. The predicted amounts of propene remaining after the reaction is quenched, and the remaining levels of C_2H_4 and C_2H_2 agree very well with the measured data. Predicted levels of H_2 and CH_4 are slightly too low, while levels of C_2H_6 are slightly high. In a preliminary series of calculations before Reactions 162 and 163 were included in the mechanism, predicted levels of methane and C_3H_4 were much too low. Combined with similar underpredictions of methane levels in the flow reactor simulations, it appeared likely that the model was omitting an important path for methane formation, or that an existing path had an incorrect rate in Table 1. An initiation reaction of the form

$$C_3H_6 = C_3H_4 + H_2$$
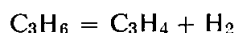
directly producing C_3H_4, with a rate chosen by analogy with that of Reaction 55

$$C_2H_4 + M = C_2H_2 + H_2 + M \tag{55}$$
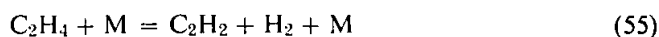
had very little effect on computed levels of C_3H_4. The computed models, particularly those with relatively small amounts of propene conversion, had significant amounts of allyl radicals present, often more than the computed amounts of C_3H_4, and appreciable amounts of butene, as well as methyl and other radical species. Inclusion of Reactions 162 and 163

$$C_3H_5 + \quad H \quad = C_3H_4 + H_2 \tag{162}$$

$$C_3H_5 + CH_3 = C_3H_4 + CH_4 \tag{163}$$
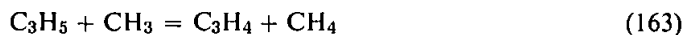
with assumed rate expressions given in Table I resulted in significant improvements in predicted CH_4 and C_3H_4 levels. As we noted earlier, the stability of the allyl radical makes it likely that reactions between it and other radical species will be particularly important, and very little direct experimental information at temperatures above 1000 K is available on such reactions. There were no experimental studies of propene oxidation available for analysis in which species concentrations of C_3H_4 or

C_3H_5 had been measured, so it was not possible to include reactions such as

$$C_3H_5 + O = products$$

$$C_3H_5 + OH = products$$
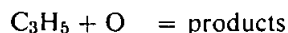
in the detailed mechanism, but it is probable that such reactions consume the majority of the allyl radicals during propene oxidation rather than the postulated model Reaction 138 with O_2. The conversion of radical species, particularly allyl and methyl radicals, to C_3H_4 and other stable compounds during the quenching period in the single pulse shock tube experiments may account for some of the discrepancies in the predicted amounts of several pyrolysis products. In addition, experimental uncertainties may account for other differences; in some of the individual shock results, as much as 30 percent of the initial fuel is unaccounted for in the tabulated experimental product species distributions.

APPLICATIONS

The present reaction mechanism has been used to predict propane and propene oxidation in two important practical environments, laminar flames and detonation waves. These results have been described in detail in other papers (Westbrook and Pitz, 1983a, 1983b; Westbrook et al., 1983b) but the overall conclusions can be summarized here since they provide additional tests of the reaction mechanism.

In laminar premixed fuel–air mixtures, the mechanism of Table I predicts a burning velocity S_u of 41 cm/sec for stoichiometric C_3H_8–air at atmospheric pressure and an unburned gas temperature of 300 K, and a burning velocity of 47 cm/sec for a comparable C_3H_6–air mixture. In addition, numerical predictions were made of the variations of S_u with equivalence ratio, pressure, and unburned gas temperature for propane–air. All of these results agree very well with available experimental burning velocity data.

In a number of modeling studies (Atkinson et al., 1980; Westbrook, 1982; Westbrook and Urtiew, 1983), it has been demonstrated that computed induction times can be related to critical detonation parameters, including lean and rich limits to detonability and minimum initiation energy for detonation. This type of analysis, using the reaction mechanism in Table I (Westbrook et al., 1983b) indicated that propane–air and propane–O_2 mixtures were only slightly more detonable than corresponding ethane–oxidizer mixtures, in agreement with experimental results (Matsui and Lee, 1979).

It has been observed experimentally (Lifshitz et al., 1971; Crossley et al., 1972) that the addition of small amounts of propane to methane–oxygen–argon mixtures in shock tubes provides a significant reduction in the observed delay time. The same type of effect has been observed when ethane is the additive (Bull et al., 1979; Nicholls, et al., 1979; Vandermolen and Nicholls, 1979; Eubank et al., 1981), and modeling analysis (Westbrook, 1979) has shown that the additive provides radical species, particularly H atoms, at a much greater rate than does the methane–oxidizer mixture alone. An important factor is that methyl radicals produced from methane do not oxidize rapidly and do not decompose to provide H atoms, while ethyl radicals produced from ethane decompose rapidly through Reaction 52. The H atoms from Reaction 52 then provide very early chain branching by means of Reaction 1, resulting in an overall acceleration of the ignition process.

Computational studies (Westbrook and Pitz, 1983a) of the sensitization of methane-oxidizer mixtures by the addition of propane, using the mechanism in Table I, showed that propane has a sensitizing effect very similar to that of ethane. When propane is present, H atoms are produced primarily from iC_3H_7 by Reaction 99. Further modeling analysis indicates that the existence of small amounts of propane in natural gas (typically 80–95% CH_4/5–10% C_2H_6/1–4% C_3H_8) can have a significant influence on its ignition and detonation properties.

ACKNOWLEDGEMENTS

REFERENCES

Al-Alami, M. Z., and Kiefer, J. H. (1983). Shock tube study of propane pyrolysis. Rate of initial dissociation from 1400 to 2300 K. *J. Phys. Chem.* **87**, 499.

Allara, D. L., and Edelson, D. (1975). A computational modeling study of the low-temperature pyrolysis of *n*-alkanes; mechanisms of propane, *n*-butane, and *n*-pentane pyrolyses. *Int. J. Chem. Kinet.* **7**, 479.

Allara, D. L., and Shaw, R. (1980). A compilation of kinetic parameters for the thermal degradation of *n*-alkane molecules. *J. Phys. Chem. Ref. Data* **9**, 523.

Amano, A., and Uchiyama, M. (1963). Thermal hydrogenolysis of propylene. *J. Phys. Chem.* **67**, 1242.

Amano, A., and Uchiyama, M. (1964). Mechanism of the pyrolysis of propylene: The formation of allene. *J. Phys. Chem.* **68**, 1133.

Aronowitz, D., Santoro, R. J., Dryer, F. L., and Glassman, I. (1979). Kinetics of the oxidation of methanol: experimental results, semi-global modeling, and mechanistic concepts. *Seventeenth Symposium (International) on Combustion*, p. 633, The Combustion Institute, Pittsburgh.

Atkinson, R., and Pitts, J. N. (1978). Kinetics of the reactions of the OH radical with HCHO and CH_3CHO over the temperature range 299–426 K. *J. Chem. Phys.* **68**, 3581.

Atkinson, R., Bull, D. C., and Shuff, P. J. (1980). Initiation of spherical detonation in hydrogen/air. *Combustion and Flame* **39**, 287.

Bahn, G. S. (1973). Approximate thermochemical tables for some C–H and C–H–O species. NASA report NASA-CR-2178.

Baker, R. R., Baldwin, R. R., and Walker, R. W. (1970). Addition of C_3H_8, *n*- and *i*-C_4H_{10} to slowly reacting mixtures of hydrogen and oxygen at 480 C. *Trans Farad. Soc.* **66**, 2812.

Bakh, G., Novak, Z., Korochuk, S. I., and Kalinenko, R. A. (1974). The role of hydrogen atoms and methyl radicals in the radiolysis of mixtures of alkane and alkene hydrocarbons. *Kin. i Katal.* **15**, 1103.

Baldwin, R. R., Hopkins, D. E., Norris, A. C., and Walker, R. W. (1970). Addition of methane to slowly reacting hydrogen–oxygen mixtures: reactions of methyl radicals. *Combustion and Flame* **15**, 33.

Baldwin, R. R., and Walker, R. W. (1973). Problems and progress in hydrocarbon oxidation. *Fourteenth Symposium (International) on Combustion*, p. 241, The Combustion Institute, Pittsburgh.

Baldwin, R. R., Bennett, J. P., and Walker, R. W. (1977). Rate constants for elementary steps in hydrocarbon oxidation. *Sixteenth Symposium (International) on Combustion*, p. 1041, The Combustion Institute, Pittsburgh.

Baulch, D. L., Drysdale, D. D., and Horne, D. G. (1973a). An assessment of rate data for high temperature systems. *Fourteenth Symposium (International) on Combustion*, p. 107, The Combustion Institute, Pittsburgh.

Baulch, D. L., Drysdale, D. D., Horne, D. G., and Lloyd, A. C. (1973b). *Evaluated Kinetic Data for High Temperature Reactions*, vol. 1, Butterworths, London.

Baulch, D. L., and Drysdale, D. D. (1974). An evaluation of the rate data for the reaction $CO + OH \rightarrow CO_2 + H$. *Combustion and Flame* 23, 215.

Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. (1976). *Evaluated Kinetic Data for High Temperature Reactions*, vol. 3. Butterworths, London.

Benson, S. W., and Haugen, G. R. (1967). Mechanisms for some high-temperature gas-phase reactions of ethylene, acetylene, and butadiene. *J. Phys. Chem.* 71, 1735.

Berkley, R. E., Woodall, G. N. C., Strauss, O. P., and Gunning, H. E. (1969). Arrhenius parameters for the reaction of propyl radicals with propane. *Canad. J. Chem.* 47, 3305.

Bowman, C. T. (1970). An experimental and analytical investigation of the high-temperature oxidation mechanisms of hydrocarbon fuels. *Combustion Science and Technology* 2, 161.

Bowman, C. T. (1975). Non-equilibrium radical concentrations in shock-initiated methane oxidation. *Fifteenth Symposium (International) on Combustion*, p. 869, The Combustion Institute, Pittsburgh.

Brabbs, T. A., and Brokaw, R. S. (1975). Shock tube measurements of specific reaction rates in the branched chain CH_4-CO-O_2 system. *Fifteenth Symposium (International) on Combustion*, p. 893, The Combustion Institute, Pittsburgh.

Browne, W. G., Porter, R. P., Verlin, J. D., and Clark, A. H. (1969). A study of acetylene-oxygen flames. *Twelfth Symposium (International) on Combustion*, p. 1035, The Combustion Institute, Pittsburgh.

Bull, D. C., Elsworth, J. E., and Hooper, G. (1979). Susceptibility of methane–ethane mixtures to gaseous detonation in air. *Combustion and Flame* 34, 327.

Burcat, A., Scheller, K., and Lifshitz, A. (1971a). Shock tube investigation of comparative ignition delay times for C_1-C_5 alkanes. *Combustion and Flame* 16, 29.

Burcat, A., Lifshitz, A., Scheller, K., and Skinner, G. B. (1971b). Shock tube investigation of ignition in propane-oxygen-argon mixtures. *Thirteenth Symposium (International) on Combustion*, p. 745, The Combustion Institute, Pittsburgh.

Burcat, A. (1975). Cracking of propylene in a shock tube. *Fuel* 54, 87.

Camilleri, P., Marshall, R. M., and Purnell, H. (1975). Arrhenius parameters for the unimolecular decomposition of azomethane and *n*-propyl and isopropyl radicals and for methyl radical attack on propane. *J. Chem. Soc. Faraday Trans. I* 71, 1491.

Cathonnet, M., Boettner, J. C., and James, H. (1981). Experimental study and numerical modeling of high temperature oxidation of propane and *n*-butane. *Eighteenth Symposium (International) on Combustion*, p. 903, The Combustion Institute, Pittsburgh.

Chappell, G. A., and Shaw, H. (1968). A shock tube study of the pyrolysis of propylene. Kinetics of the vinyl–methyl bond rupture. *J. Phys. Chem.* 72, 4672.

Chiang, C., and Skinner, G. B. (1981). Resonance absorption measurements of atom concentrations in reacting gas mixtures—5. Pyrolysis of C_3H_8 and C_3D_8 behind shock waves. *Eighteenth Symposium (International) on Combustion*, p. 915, The Combustion Institute, Pittsburgh.

Clark, T. C., and Dove, J. E. (1973). Examination of possible non-Arrhenius behavior in the reactions $H + C_2H_6 \rightarrow H_2 + C_2H_5$, $H + CH_4 \rightarrow H_2 + CH_3$, $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$. *Canad. J. Chem.* 51, 2147.

Colket, M. D., Naegeli, D. W., and Glassman, I. (1977). High temperature oxidation of acetaldehyde. *Sixteenth Syposium (International) on Combustion*, p. 1023, The Combustion Institute, Pittsburgh.

Crossley, R. W., Dorko, E. A., Burcat, A., and Skinner, G. B. (1972). The effect of higher alkanes on the ignition of methane–oxygen–argon mixtures in shock tubes. *Combustion and Flame* 19, 373.

Cvetanovic, R. J., and Irwin, R. S. (1967). Rates of addition of methyl radicals to olefins in the gas phase. *J. Chem. Phys.* 46, 1694.

Davis, D. D., Huie, R. E., Kurylo, M. J., and Braun, W. (1972). Absolute rate constants for the reaction of atomic oxygen with ethylene over the temperature range 232–500 K. *J. Chem. Phys.* 56, 4868.

Dean, A. M., Johnson, R. L., and Steiner, D. C. (1980). Shock tube studies of formaldehyde oxidation. *Combustion and Flame* 37, 41.

Dryer, F. L. (1972). High temperature oxidation of carbon monoxide and methane in a turbulent flow reactor. Princeton University Ph.D. thesis, Department of Aerospace and Mechanical Sciences.

Dryer, F. L., and Glassman, I. (1979). Combustion chemistry of chain hydrocarbons. *Prog. Astro. and Aero.* **62**, 255.

Edelson, D., and Allara, D. L. (1980). A computational analysis of the alkane pyrolysis mechanism: Sensitivity analysis of individual reaction steps. *Int. J. Chem. Kinet.* **12**, 605.

Engleman, V. S. (1976). Survey and evaluation of kinetic data on reactions in methane/air combustion. EPA Report EPA-600/2-76-003.

Eubank, C. S., Rabinowitz, M. J., Gardiner, W. C., Jr., and Zellner, R. E. (1981). Shock-initiated ignition of natural gas-air mixtures. *Eighteenth Symposium (International) on Combustion*, p. 1767, The Combustion Institute, Pittsburgh.

Falconer, W. E., Rabinovitch, B. S., and Cvetanovic, R. J. (1963). Unimolecular decomposition of chemically activated propyl radicals. Normal intermolecular secondary kinetic isotope effect. *J. Chem. Phys.* **39**, 40.

Fenimore, C. P. (1969). Destruction of methane in water gas by reaction of CH_3 with OH radicals. *Twelfth Symposium (International) on Combustion*, p. 463, The Combustion Institute, Pittsburgh.

Flowers, M. C. (1977). Kinetics of the thermal gas-phase decomposition of 1,2-epoxypropane. *J. Chem. Soc. Faraday Trans. I* **73**, 1927.

Gardiner, W. C., Jr., and Walker, B. F. (1968). Source of Schlieren signals from acetylene combustion in shock waves. *J. Chem. Phys.* **48**, 5279.

Gardiner, W. C., Jr., McFarland, M., Morinaga, K., Takeyama, T., and Walker, B. F. (1971). Initiation rate for shock-heated hydrogen-oxygen-carbon monoxide-argon mixtures as determined by OH induction time measurements. *J. Phys. Chem.* **75**, 1504.

Gray, P., and Herod, A. A. (1968). Methyl radical reactions with isopropanol and methanol, their ethers, and their deuterated derivatives. *Trans. Faraday Soc.* **64**, 2723.

Greiner, N. R. (1970). Hydroxyl radical kinetics by kinetic spectroscopy. VI. Reactions with alkanes in the range 300–500 K. *J. Chem. Phys.* **53**, 1070.

Hartig, R., Troe, J., and Wagner, H. Gg. (1971). Thermal decomposition of methane behind reflected shock waves. *Thirteenth Symposium (International) on Combustion*, p. 147, The Combustion Institute, Pittsburgh.

Hautman, D. J. (1980). Pyrolysis and oxidation kinetic mechanisms for propane. Ph.D. thesis, Princeton University, Department of Aerospace and Mechanical Sciences.

Hautman, D. J., Santoro, R. J., Dryer, F. L., and Glassman, I. (1981). An overall and detailed kinetic study of the pyrolysis of propane. *Int. J. Chem. Kinet.* **13**, 149.

Herriott, G. E., Eckert, R. E., and Albright, L. F. (1972). Kinetics of propane pyrolysis. *A. I. Chem. Eng. J.* **18**, 84.

Herron, J. T. (1969). An evaluation of rate data for the reactions of atomic oxygen with methane and ethane. *Int. J. Chem. Kinet.* **1**, 527.

Herron, J. T., and Huie, R. E. (1973). Rate constants for the reactions of atomic oxygen with organic compounds in the gas phase. *J. Phys. Chem. Ref. Data* **2**, 467.

Huie, R. E., and Herron, J. T. (1975). Reaction of atomic oxygen (O^3P) with organic compounds. *Progress in Reaction Kinetics*, vol. 8, Part 1, p. 1. Oxford: Pergamon Press.

Illes, V. (1971). The pyrolysis of gaseous hydrocarbons, III. Kinetics and mechanism of the thermal decomposition of propane. *Acta Chim. Acad. Sci. Hung.* **67**, 41.

Jachimowski, C. J. (1977). An experimental and analytical study of acetylene and ethylene oxidation behind shock waves. *Combustion and Flame* **29**, 55.

Jackson, W. M., and McNesby, J. R. (1961). Photolysis of acetone-d_6 in the presence of propane-2,2-d_2. Decomposition of the *n*-propyl radical. *J. Amer. Chem. Soc.* **83**, 4891.

Jackson, W. M., and McNesby, J. R. (1962). Thermal isomerization of isopropyl-1,1,1-d_3 radicals. *J. Chem. Phys.* **36**, 2272.

JANAF Thermochemical Tables (1970). D. K. Stull *et al.* (Eds.). Dow Chemical Company, Midland, Michigan.

Jenkins, D. R., Yumlu, V. S., and Spalding, D. B. (1967). Combustion of hydrogen and oxygen in a steady flow adiabatic stirred reactor. *Eleventh Symposium (International) on Combustion*, p. 779, The Combustion Institute, Pittsburgh.

Kallend, A. S., Purnell, J. H., and Shurlock, B. C. (1967). The pyrolysis of propylene. *Proc. Roy. Soc., Ser. A* **300**, 120.

Kerr, J. A., and Trotman-Dickenson, A. F. (1959). The reactions of alkyl radicals. Part 2. *s*-propyl radicals from the photolysis of isobutyraldehyde. *Trans. Faraday Soc.* **55**, 921.

Kiefer, J. H., Al-Alami, M. Z., and Budach, K. A. (1982). A shock tube, laser schlieren study of propene pyrolysis at high temperature. *J. Phys. Chem.* **86**, 808.

Koike, T., and Gardiner, W. C., Jr. (1980). Thermal decomposition of propane. *J. Phys. Chem.* **84**, 2005.

Laidler, K. J., and Wojciechowski, B. W. (1960). Kinetics of the thermal decomposition of propylene, and of propylene-inhibited hydrocarbon decompositions. *Proc. Roy. Soc., Ser. A* **259**, 257.

Laidler, K. J., Sagért, N. H., and Wojciechowski, B. W. (1962). Kinetics and mechanisms of the thermal decomposition of propane. I. The uninhibited reaction. *Proc. Roy. Soc., Ser. A* **270**, 242.

Layokun, S. K. (1979). Oxidative pyrolysis of propane. *Ind. Eng. Chem. Process Des. Dev.* **18**, 241.

Layokun, S. K., and Slater, D. H. (1979). Mechanism and kinetics of propane pyrolysis. *Ind. Eng. Chem. Process Des. Dev.* **18**, 232.

Leathard, D. A., and Purnell, J. H. (1968). The self-inhibited pyrolysis of propane at small extents of reaction. *Proc. Roy. Soc. A* **305**, 517.

Lede, J., and Villermaux, J. (1978). Mésure de la constante de vitesse de réaction des atomes d'hydrogène sur l'éthane et le propane en réacteurs tubulaire et parfaitement agite ouverts. *Canad. J. Chem.* **56**, 392.

LeFevre, H. F., Meagher, J. F., and Timmons, R. B. (1972). The kinetics of the reactions of $O(^3P)$ atoms with dimethyl ether and methanol. *Int. J. Chem. Kinet.* **4**, 103.

Levy, J. M., Taylor, B. R., Longwell, J. P., and Sarofim, A. F. (1983). C_1 and C_2 chemistry in rich-mixture ethylene-air flames. *Nineteenth Symposium (International) on Combustion,* p. 167, The Combustion Institute, Pittsburgh.

Lifshitz, A., Scheller, K., Burcat, A., and Skinner, G. B. (1971). Shock tube investigation of ignition in methane–oxygen–argon mixtures. *Combustion and Flame* **16**, 311.

Lifshitz, A., Scheller, K., and Burcat, A. (1973). Decomposition of propane behind reflected shocks in a single pulse shock tube. *Proc. Seventh Int. Shock Tube Symp.,* 690.

Lifshitz, A., and Frenklach, M. (1975). Mechanism of the high temperature decomposition of propane. *J. Phys. Chem.* **79**, 686.

Lloyd, A. C. (1974). Evaluated and estimated kinetic data for phase reactions of the hydroperoxyl radical. *Int. J. Chem. Kinet.* **6**, 169.

Matsui, H., and Lee, J. H. (1979). On the measure of the relative detonation hazards of gaseous fuel–oxygen and air mixtures. *Seventeenth Symposium (International) on Combustion,* p. 1269, The Combustion Institute, Pittsburgh.

Mayer, S. W., Schieler, L., and Johnston, H. S. (1967). Computation of high temperature rate constants for bimolecular reaction of combustion products. *Eleventh Symposium (International) on Combustion,* p. 837, The Combustion Institute, Pittsburgh.

McLain, A. G., and Jachimowski, C. J. (1977). Chemical kinetic modeling of propane oxidation behind shock waves. NASA TN D-8501.

McMillen, D. F., and Golden, D. M. (1982). Hydrocarbon bond dissociation energies. *Ann. Rev. Phys. Chem.* **33**, 493.

Michael, J. V., Nava, D. F., Payne, W. A., and Stief, L. J. (1979). Absolute rate constants for the reaction of atomic hydrogen with ketene from 298 to 500 K. *J. Chem. Phys.* **70**, 5222.

Miller, J. A., Mitchell, R. E., Smooke, M. D., and Kee, R. J. (1983). Toward a comprehensive chemical kinetic mechanism for the oxidation of acetylene: Comparison of model predictions with results from flame and shock tube experiments. *Nineteenth Symposium (International) on Combustion,* p. 181, The Combustion Institute, Pittsburgh.

Moretti, G. (1965). A new technique for the numerical analysis of nonequilibrium flows. *AIAA J.* **3**, 223.

Nicholls, J. A., Sichel, M., Gabrijel, Z., Oza, R. D., and Vandermolen, R. (1979). Detonability of unconfined natural gas–air clouds. *Seventeenth Symposium (International) on Combustion,* p. 1223, The Combustion Institute, Pittsburgh.

Niki, H., Daby, E. E., and Weinstock, B. (1969). Mass spectrometric study of the kinetics and mechanism of the ethylene-atomic oxygen reaction by the discharge-flow technique at 300 K. *Twelfth Symposium (International) on Combustion,* p. 277, The Combustion Institute, Pittsburgh.

Olson, D. B., Tanzawa, T., and Gardiner, W. C., Jr. (1979). Thermal decomposition of ethane. *Int. J. Chem. Kinet.* **11**, 23.

Pacey, P. D. (1973). Detection of methyl radicals in flow pyrolysis by ultraviolet spectroscopy. *Chem. Phys. Lett.* **23**, 394.

Papic, M. M., and Laidler, K. J. (1971). Kinetics of the mercury-photosensitized decomposition of propane. Part II. Reactions of the propyl radicals. *Canad. J. Chem.* **49**, 549.

Peeters, J., and Mahnen, G. (1973). Reaction mechanisms and rate constants of elementary steps in methane–oxygen flames. *Fourteenth Symposium (International) on Combustion*, p. 133, The Combustion Institute, Pittsburgh.

Peeters, J., and Vinckier, C. (1975). Production of chemi-ions and formation of CH and CH_2 radicals in methane–oxygen and ethylene–oxygen flames. *Fifteenth Symposium (International) on Combustion*, p. 969, The Combustion Institute, Pittsburgh.

Perry, R. A. (1983). Absolute rate constants for the reaction of $O(^3P)$ atoms with ethylene, propylene, and propylene-d_6 over the temperature range 258–861 K. Presented at the 1983 Spring Meeting of the Western States Section of The Combustion Institute, Jet Propulsion Institute, Pasadena, California, April 1983.

Simmie, J. M., Gardiner, W. C., Jr., and Eubank, C. S. (1982). Falloff behavior in propane thermal decomposition at high temperature. *J. Phys. Chem.* **86**, 799.

Simonaitis, R., and Heicklen, J. (1972). Kinetics and mechanism of the reaction of O with carbon monoxide. *J. Chem. Phys.* **56**, 2004.

Skinner, G. B., Lifshitz, A., Scheller, K., and Burcat, A. (1972). Kinetics of methane oxidation. *J. Chem. Phys.* **56**, 3853.

Sundaram, K. M., and Froment, G. F. (1978). Modeling of thermal cracking kinetics. 3. Radical mechanisms for the pyrolysis of simple paraffins, olefins, and their mixtures. *Ind. Eng. Chem. Fundam.* **17**, 174.

Szwarc, M. (1949). The kinetics of the thermal decomposition of propylene. *J. Chem. Phys.* **17**, 284.

Tanzawa, T., and Gardiner, W. C., Jr. (1979). Thermal decomposition of acetylene. *Seventeenth Symposium (International) on Combustion*, p. 563, The Combustion Institute, Pittsburgh.

Tanzawa, T., and Gardiner, W. C., Jr. (1980). Thermal decomposition of ethylene. *Combustion and Flame* **39**, 241.

Trotman-Dickenson, A. F. (1965). The abstraction of hydrogen atoms by free radicals. *Advances in Free Radical Chemistry*, **1**.

Tsang, W. (1969). Thermal decomposition of 3,4-dimethylpentene-1, 2,3,3-trimethylpentane, 3,3-dimethylpentane, and isobutylbenzene in a single pulse shock tube. *Int. J. Chem. Kinet.* **1**, 245.

Tully, F. P., Ravishankara, A. R., and Carr, K. (1983). Kinetic study of the reactions of the hydroxyl radical with ethane and propane. *Int. J. Chem. Kinet.* **15**, 1111.

Tunder, R., Mayer, S., Cook, E., and Schieler, L. (1966). Aerospace Corporation Report TR-1001 (9210-02)-1 (AD813485).

Vandermolen, R., and Nicholls, J. A. (1979). Blast wave initiation energy for the detonation of methane–ethane mixtures. *Combustion Science and Technology* **21**, 75.

Vandooren, J., and Van Tiggelen, P. J. (1977). Reaction mechanisms of combustion in low pressure acetylene–oxygen flames. *Sixteenth Symposium (International) on Combustion*, p. 1133, The Combustion Institute, Pittsburgh.

Walker, R. W. (1975). *Reaction Kinetics*, vol. 1, p. 161, London: The Chemical Society.

Warnatz, J. (1981). The structure of laminar alkane-, alkene-, and acetylene flames. *Eighteenth Symposium (International) on Combustion*, p. 369, The Combustion Institute, Pittsburgh.

Warnatz, J. (1983a). Survey of rate coefficients in the C/H/O system. To be published.

Warnatz, J. (1983b). The mechanism of high temperature combustion of propane and butane. *Combustion Science and Technology*, to appear.

Warnatz, J., Bockhorn, H., Moser, A., and Wenz, H. W. (1983). Experimental investigations and computational simulation of acetylene–oxygen flames from near-stoichiometric to sooting conditions. *Nineteenth Symposium (International) on Combustion*, p. 197, The Combustion Institute, Pittsburgh.

Watkins, K. W., and Word, W. W. (1974). Addition of methyl radicals to carbon monoxide: chemically and thermally activated decomposition of acetyl radicals. *Int. J. Chem. Kinet.* **6**, 855.

Westbrook, C. K., Creighton, J., Lund, C., and Dryer, F. L. (1977). A numerical model of chemical kinetics of combustion in a turbulent flow reactor. *J. Phys. Chem.* **81**, 2542.

Westbrook, C. K. (1979). An analytical study of the shock tube ignition of mixtures of methane and ethane. *Combust. Sci. and Technol.* **20**, 5.

Westbrook, C. K., and Dryer, F. L. (1979). A comprehensive mechanism for methanol oxidation. *Combustion Science and Technology* **20**, 125.

Westbrook, C. K., and Dryer, F. L. (1981). Chemical kinetics and the modeling of combustion processes. *Eighteenth Symposium (International) on Combustion*, p. 749, The Combustion Institute, Pittsburgh.

Westbrook, C. K. (1982). Chemical kinetics of hydrocarbon oxidation in gaseous detonations. *Combustion and Flame* **46**, 191.

Westbrook, C. K., and Dryer, F. L. (1984). Chemical kinetics modeling of hydrocarbon combustion, *Progress in Energy and Combustion Science*, to be published.

Westbrook, C. K., and Urtiew, P. A. (1983). Chemical kinetic prediction of critical parameters in gaseous detonations. *Nineteenth Symposium (International) on Combustion*, p. 615, The Combustion Institute, Pittsburgh.

Westbrook, C. K., and Pitz, W. J. (1983a). Effects of propane on ignition of methane–ethane–air mixtures. *Combustion Science and Technology* **33**, 315.

Westbrook, C. K., and Pitz, W. J. (1983b). Prediction of laminar flame properties of propane–air mixtures, *Ninth International Colloquium on Dynamics of Explosions and Reactive Systems*, in press.

Westbrook, C. K., Dryer, F. L., and Schug, K. P. (1983a). A comprehensive mechanism for the pyrolysis and oxidation of ethylene. *Nineteenth Symposium (International) on Combustion*, p. 153, The Combustion Institute, Pittsburgh.

Westbrook, C. K., Pitz, W. J., and Urtiew, P. A. (1983b). Chemical kinetics of propane oxidation in gaseous detonations. *Ninth International Colloquium on Dynamics of Explosions and Reactive Systems*, in press.

Westenberg, A. A., and de Haas, N. (1972). Relative rate constants for $O + HCO \rightarrow OH + CO$ and $O + HCO \rightarrow H + CO_2$. *J. Phys. Chem.* **76**, 2215.

Yang, K. (1963). Free radical reactions initiated by ionizing radiations. III. Paraffin reactivities in hydrogen atom abstraction reactions. *J. Phys. Chem.* **67**, 562.

Yano, T. (1977). Shock tube study of thermal decomposition of propene in the presence of deuterium. *Int. J. Chem. Kinet.* **9**, 725.

Zellner, R., and Steinert, W. (1976). A flash photolysis study of the rate of the reaction $OH + CH_4 \rightarrow CH_3 + H_2O$ over an extended temperature range. *Int. J. Chem. Kinet.* **8**, 397.